

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~~likely contributes to the formation of secondary organic aerosol (SOA) from biogenic volatile organic compounds. ~~Still, the, but~~ quantitative and mechanistic data for such precursors are limited. In this study, the aqueous-phase reactions of three atmospherically relevant, ~~saturated~~ terpenoidic alcohols (TAs)—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~~modelling. The objectives were to elucidate reaction mechanisms, identify ~~oxidation~~major products, and quantify yields of aqueous SOA (aqSOA) 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~~low-volatility terpenoidic acids formed as ~~second~~higher-generation products, providing new evidence for the formation of low-volatility compounds from aqueous OH ~~reaction~~reactions with TAs. The molar yields of quantified products approached unity (~~0.88–0.99~~), indicating ~~near-complete closure~~within the estimated uncertainties, which were ca. 30%, primarily due to the use of the ~~carbon-balance-surrogate standards~~. Based on these data, explicit kinetic box models were developed ~~that~~, successfully ~~reproduced~~reproducing the measured temporal evolution of reactants. Modelled aqSOA yields ranged from 10% to 70%, depending on liquid water content and reaction ~~coordinate~~progress, representing the first quantitative estimates for the three TAs under investigation. The results 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 and Deb and Pervez, 2021). Because about Fine atmospheric particulate matter (PM) - solid and liquid particles suspended in the air - affects the climate, air quality, and harms human health (Jo et al., 2023). Aerosols with aerodynamic diameter $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) absorb and scatter solar radiation and act as cloud condensation nuclei (CCN) and ice nuclei (IN), thus influencing the formation and albedo of clouds and Earth's hydrological cycle (Shrivastava et al., 2017). Furthermore, exposure to $\text{PM}_{2.5}$ negatively impacts human health and is associated with various cardiovascular and respiratory conditions (Wei et al., 2019).

Fine atmospheric PM is composed of various materials, often with a dominant contribution of organic compounds (Jimenez et al., 2009; Kelly et al., 2018; Xu et al., 2021). The majority of organics found in fine PM are secondary in origin, formed by oxidation of volatile organic compounds (VOCs) emitted from biogenic and man-made sources, including vegetation fires (Sindelarova et al., 2022; Kelly et al., 2018). Furthermore, because ca. 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 and Deb and Pervez, 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) atmospheric oxidation of biogenic VOCs (BVOCs), mainly isoprene (major BVOC) and monoterpenes (Sindelarova et al., 2022), is a well-known source of secondary organic aerosols (SOAs) (Mahilang and Deb and Pervez, 2021; Shrivastava et al., 2017). In fact, the production of SOAs from BVOCs is currently estimated at $\sim 73.6 - 140 \text{ Tg} \text{ yr}^{-1}$ (Hodzic et al., 2016; Kelly et al., 2018; Spracklen et al., 2011), contributing up to 90% of fine PM mass (Jimenez et al., 2009; Zhang et al., 2005; Xu et al., 2021; Kanakidou et al., 2005; Fuzzi et al., 2015).

Isoprene (C_5H_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 (gas 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: α and β -pinene and limonene (Wang et al., 2024; Sindelarova et al., 2022; Kamens and Jaoui, 2001).

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Production of SOAs from these BVOCs is initiated primarily by atmospherically abundant oxidants: ozone (O_3), hydroxyl, and nitrate (NO_3) radicals (Mahilang and Deb and Pervez, 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 monoterpene SOAs include terpenoic acids (TACs), non-acidic monoterpene oligomers (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) In addition to isoprene and monoterpenes, oxygenated monoterpene oligomers (MTDs) also contribute to BVOCs emissions (Guenther et al., 2012). For instance, the global emissions of 31 MTDs were estimated at 14.9 Tg yr^{-1} for (Guenther et al., 2012), compared with α -pinene (the most abundant monoterpene) and isoprene emissions of 27 and 440 Tg yr^{-1} , respectively (Sindelarova et al., 2022). Furthermore, emissions of all terpenoic alcohols (TAs), of which fenchol (FCH), borneol (BNL) and menthol (MTH) were the focus of this work (Fig. 1), can be estimated at 15 Tg yr^{-1} , accounting for 9% of reactive VOCs other than monoterpenes (Griffin et al., 1999).

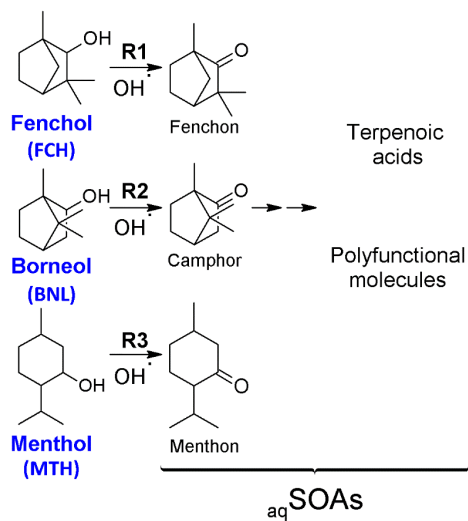


Figure 1: Precursors and reactions investigated.

, does not provide a complete picture of the formation and evolution of SOAs (Su and Cheng and Pöschl, 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 and Cheng and Pöschl, 2020; Lim et al., 2010; Carlton et al., 2020; Ervens, 2015; Ervens et al.,

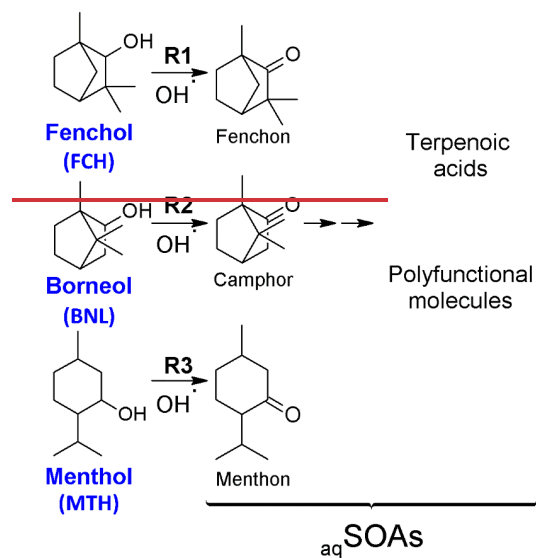
2018). Consequently, for over a decade, there has been an increasing focus on the still incompletely characterized aqueous reaction in clouds, fogs, haze, and some aerosols in the context of the formation and processing of SOAs (Su and Cheng and Pöschl, 2020; Carlton et al., 2020; Lim et al., 2010; Ervens, 2015). Reactions of WSOs 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 and Turpin and Weber, 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 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 and Cheng and Pöschl, 2020; Tsui and Woo and Meneill, 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 incomplete, making it difficult to constrain the climate forcing of fine aerosols (Icep, 2023; Tsingaridis 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 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 and Al-Sharafi and Gierczak, 2019; Amorim et al., 2021; Enami and Sakamoto, 2016b; Huang et al., 2018; Otto and Schaefer and Herrmann, 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 HOMs following gas and aqueous oxidation by OH and O_3 (Leviss and Ry and Hinrichs, 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 ($H^{cc} \sim 1 \times 10^6$) (Episuite 4.11). 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, mechanisms, and $_{aq}$ SOAs yields from R1-3.



The three TAs that were the focus of this work are among the major components of various plant oils (Kamatou et al., 2013; Ghaffari and Rahimmalek and Sabzalian, 2019; Yassaa and Youcef Meklati and Cecinato, 2000). FCH and BNL were identified in essential oils of *Tarchonanthus camphoratus*, *Eucalyptus globulus*, and *Cedrus atlantica* (Yassaa and Youcef Meklati and Cecinato, 2000; Matasyoh et al., 2007), while MTH is produced by a wide variety of flowering plants from the *Mentha* genus (Kamatou et al., 2013). The fluxes of TAs investigated in this work from plants are difficult to constrain, as estimated emissions of all MTDs are very often lumped together (Fares et al., 2011; Kim et al., 2010). As such, the emissions of MTDs from plants range from 0.15 to 4.6 μg per g of dry weight per h ($\mu\text{g g}^{-1} \text{h}^{-1}$) (Fares et al., 2011; Kim et al., 2010), and the emissions of BNL and FCH from pine and from broad-leaved trees were reported to increase following mechanical and insect damage and thermal stress (Joutsensaari et al., 2015; Yuan et al., 2025; Kivimäenpää et al., 2016). These data strongly indicate that globally widespread plant species are a significant source of TAs, alongside other MTDs (Mckinney et al., 2011). The atmospheric abundance of MTD is further supported by field studies reporting ambient concentrations between 0.05 and 10 ppb in forested and agricultural regions (Li et al., 2020; Gentner et al., 2014; Fares et al., 2012). In addition to biogenic emissions, MTDs, including FCH and BNL, are commonly detected in biomass burning (BB) smoke, with measured ambient concentrations between 0.022 and 3.17 $\mu\text{g m}^{-3}$ (Hatch et al., 2019; Dickinson et al., 2022). For these reasons, emissions of TAs and other MTDs from biomass burning and vegetation are likely to increase in the foreseeable future due to rising global temperatures and the increasing frequency and intensity of wildfires (Kelley et al., 2025; Abatzoglou et al., 2025; Ipcc, 2023).

Because of their high abundance of essential oils, MTDs, including TAs shown in Fig. 1, are widely utilized as fragrance and flavouring agents; in the production of cigarettes, cleaning and personal care products, food, as well as environmentally friendly insecticides (Caputi and Aprea, 2011; Bhatia and Letizia and Api, 2008; Bhatia et al., 2008; Kamatou et al., 2013). MTH, in particular, has a wide variety of industrial applications with an estimated annual consumption of about 30 000 t, exceeding natural production by about 50% (Kamatou et al., 2013; Shakil et al., 2026). Moreover, MTH and BNL are used in the pharmaceutical industry due to their antimicrobial, antiviral, and anticancer properties (Kamatou et al., 2013; Shakil et al., 2026). Relatively large quantities of MTD are also emitted from herbs and spices during cooking (Klein et al., 2016). Hence, the reported concentrations of MTDs and TAs in indoor air range from a few up to 900 $\mu\text{g m}^{-3}$, primarily due to the use of cleaning products and air fresheners (Singer et al., 2006; Angulo Milhem et al., 2021; Rosales et al., 2022).

In the atmosphere, TAs can influence the oxidizing capacity, tropospheric ozone (O_3) formation, and undergo atmospheric oxidation, forming SOAs, alongside other BVOCs (Mellouki and Wallington and Chen, 2015; Wang et al., 2024b). The formation of SOA from BVOCs is initiated by reaction with O_3 , hydroxyl (OH), and nitrate (NO_3) radicals, generating a cascade of oxygenated, low-volatility products (Zhang et al., 2015; Kamens and Jaoui, 2001; Kourtchev et al., 2014; Mahilang and Deb and Pervez, 2021), which add to the pre-existing particle mass (Shrivastava et al., 2017; Xu et al., 2021). Because monoterpenes are non-polar hydrocarbons, the addition of even a single oxygenated moiety to their carbon skeleton results in the formation of water-soluble organic compounds (WSOCs). The WSOCs contributing to monoterpeneic SOAs include terpenoic acids (TACs), MTDs, and oligomers, some of which are classified as highly oxygenated molecules (HOMs) (Kenseth et al., 2020; Valorso et al., 2011; Yasmeen et al., 2011; Liu et al., 2023).

To date, numerous studies have focused on the formation of SOAs from the atmospherically abundant monoterpenes, primarily α/β -pinene and limonene (Wang et al., 2024a; Sindelarova et al., 2022; Kamens and Jaoui, 2001). At the same time, the mass yields of SOAs formed from the oxidation of MTDs, including BNL, are often higher than those of monoterpenes (alkenes) (Khalaj et al., 2025; Griffin et al., 1999). Because MTDs already contain at least one oxygenated moiety, they tend to produce HOMs and oligomers more efficiently following reactions with atmospheric oxidants compared with monoterpenes (Ceacero-Vega et al., 2012; Khalaj et al., 2025; Mehra et al., 2020). Indeed, gas-phase reactions of OH and chlorine atoms with MTH, FCH, and BNL resulted in the formation of various oxygenated products (Ceacero-Vega et al., 2012), including oligomers (Mehra et al., 2020), making some MTDs potentially efficient precursors of ambient and indoor SOA (Khalaj et al., 2025; Wu et al., 2024; Rosales et al., 2022).

It is now well established that the classical model involving the gas-phase oxidation of BVOCs followed by gas-particle partitioning of low-volatility organics (Pankow, 1994; Odum et al., 1996), does not provide a complete picture of the formation and evolution of SOAs (Su and Cheng and Pöschl, 2020; Carlton et al., 2020; Tsigaridis and Kanakidou, 2018; Ervens, 2015). Because liquid water is ubiquitous in the atmosphere in the form of clouds, fogs, and aqueous aerosols, oxidation of WSOCs inside and on the surface of these hydrometeors can lead to so-called aqueous SOAs ($_{\text{aq}}$ SOAs) (Su and Cheng and Pöschl, 2020; Carlton et al., 2020; Ervens, 2015). Aqueous oxidation of WSOCs in the atmosphere also involves unique species and mechanisms, distinct from the gas-phase reactions, leading to HOMs and extremely low-volatility organic compounds

(ELVOCs) (Ervens, 2015; Zhu et al., 2020; Sullivan et al., 2016; Sun et al., 2010; Ervens and Turpin and Weber, 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, producing μSOAs after water evaporation (Sullivan et al., 2016; Paglione et al., 2020; Kuang et al., 2020b). Results of field and laboratory studies also indicate that the contribution of μSOAs to the global and local organic aerosols (OAs) burden is likely significant (Paglione et al., 2020; Kuang et al., 2020b; Su and Cheng and Pöschl, 2020; Tsui and Woo and McNeill, 2019). In addition to affecting SOA formation and processing, the multiphase chemistry alters physicochemical characteristics of OAs, including composition, optical and toxicological properties, as well as CCN and IN activity (Carlton et al., 2020; Ervens, 2015; Sullivan et al., 2016; Decesari et al., 2017). 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 and Cheng and Pöschl, 2020; Carlton et al., 2020; Lim et al., 2010; Ervens, 2015). At the same time, the fundamental data necessary to parametrize multiphase chemistry of SOAs remain incomplete, making it difficult to reliably constrain the climate forcing of fine PM (Ipcc, 2023; Tsigaridis and Kanakidou, 2018).

In the atmosphere, OH (major daytime oxidant) is formed from O_3 photolysis and diffuses into aqueous particles from the gas phase (Price et al., 2025). In addition to the gas-phase formation, OH can be produced inside hydrometeors by decomposition of hydrogen peroxide (H_2O_2) via photolytic or Fenton and Fenton-like processes, greatly enhancing the oxidative capacity of some aqueous particles (Kuang et al., 2020a; Bianco et al., 2020). For these reasons, several studies have investigated the OH-initiated formation and aging of monoterpene μSOAs , focusing on individual precursors and BSOA mixtures (Witkowski and Al-Sharafi and Gierczak, 2019; Amorim et al., 2021; Enami and Sakamoto, 2016; Huang et al., 2018; Otto and Schaefer and Herrmann, 2018; Amorim et al., 2020; Witkowski et al., 2023), as many MTDs and TACs lack C=C bonds of monoterpenes, making them unreactive towards O_3 (Khalaj et al., 2025). Still, major knowledge gaps persist regarding the aqueous oxidation mechanisms and mass yields of μSOA formed through aqueous OH reactions with MTDs (Leviss and Van Ry and Hinrichs, 2016; Bleier and Elrod, 2013), as most studies published to date have often focused on TACs and acidic organosulfates (Witkowski and Al-Sharafi and Gierczak, 2019; Amorim et al., 2021; Enami and Sakamoto, 2016; Huang et al., 2018; Otto and Schaefer and Herrmann, 2018; Lai et al., 2025).

This work aimed to address knowledge gaps in μSOA formation from the OH-initiated oxidation of MTDs, focusing on reaction mechanisms and aerosol mass yields. An overarching goal was to constrain the global μSOA flux from the aqueous OH reactions with MTDs. As concluded in our previous study, FCH, BNL, and MTH can enter water-containing particles considering their dimensionless Henry’s law constants ($H^c \approx 1 \times 10^3$) (Sander, 2023). Furthermore, the estimated lifetimes indicate that these TAs can undergo aqueous reaction with OH in air masses with liquid water content (LWC) $\geq 0.1 \text{ g m}^{-3}$ at atmospherically relevant timescales.

Figure 1: Precursors and reactions investigated.

The TAs under investigation (Fig. 1) are more volatile than terpenoid diols and acids and will likely remain in the gas phase when there is no water present (Keating and Harris and Chickos, 2017). At the same time, the TAs are semi-volatile organic compounds (SVOCs) that can enter water particles ($H^c \approx 1 \times 10^3$) 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) $\geq 0.1 \text{ g m}^{-3}$ (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 and Rahimmalek and Sabzalian, 2019; Yassaa and Youcef Meklati and Cecinato, 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 Tg yr⁻¹ for 34 MTDs, compared with 66.1 Tg yr⁻¹ estimated for α -pinene (Guenther et al., 2012). Additionally, the total flux of TAs was estimated at 14.6 Tg yr⁻¹, 9% of total monoterpene emission (Griffin et al., 1999).

For these reasons, the three TAs (Fig. 1) were selected as model precursors of _{aq}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 _{aq}SOA from R1-3 (Jain et al., 2024).

(Witkowski et al., 2024). Hence, these TAs were studied in this work as potential precursors of _{aq}SOAs.

The TAs shown in Fig. 1 share structural features with many MTDs and atmospherically abundant monoterpenes, namely alkyl-substituted C₆ rings, fused with C₅ rings (Jenkin, 2004; Kamens and Jaoui, 2001; Khalaj et al., 2025). The TAs under investigation (C₁₀H₁₈O) are also suitable representative precursors for studying the formation of _{aq}SOAs from the early-stage products of monoterpenes (C₁₀H₁₆) oxidation. Many secondary MTDs, including pinaketone, sabinaketone, limonaketone, norpinone, pinanediol, or 2-hydroxy-3-pinane, retain the carbon skeleton of the parent monoterpene (Kamens and Jaoui, 2001; Bleier and Elrod, 2013; Jenkin, 2004; Glasius et al., 2000). At the same time, the addition of even a single oxygenated moiety makes such molecules sufficiently soluble in water to become a potential precursor of _{aq}SOAs (Sander, 2023).

In this work, aqueous OH reactions with FCH, BNL, and MTH (R1-R3 in Fig. 1) were carried out in a custom-built photochemical reactor (Jain et al., 2024). Analyses were performed with gas (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS) to study the formation of non-acidic products and TACs formed from R1-R3. 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. The chemical models were then combined with the H^{cc} values of the reactants to estimate the global flux of _{aq}SOAs from MTDs.

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.

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 was 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_2O_2) was a photolytic precursor of OH. The aqueous reaction solution (0.1 mL) contained a mixture of one of MTAs (0.6 mM) and H_2O_2 (0.09 M). After the reactants were dissolved, the solution was filtered through a 0.7- μm 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 μm syringe filter (PTFE) and injected. For GC/MS analyses, the reaction was carried out for 30–35 min, and progress was monitored by sampling aliquots of the reaction mixture. These samples were analyzed using gas chromatography coupled with electron ionization (GC/MS-EI) and negative chemical ionization (GC/MS-NCI) utilizing ammonia (NH_3) and methane (CH_4) as reagent gases and liquid chromatography coupled with electrospray ionization and time-of-flight mass spectrometry (LC-ESI/ToF/MS). For GC/MS-EI and GC/MS-NCI analyses, 800 μl of the reaction solution was saturated with sodium chloride and extracted with 300 μl 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. For LC-ESI/ToF/MS analyses, each aliquot was filtered through a 0.22 μm syringe filter (PTFE) and injected into the 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).

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

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In Eq. (1), [Product]_t is the concentration of a product at time t, from the onset of the reaction (in mM). Δ[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).

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

Kinetic modeling was performed with the Java version of Acuchem (Braun and Herron and Kahaner, 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 $k_{off,aq}$ 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

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).

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

In Eq. (2), _{aq}SOAs yield (% w/w) is the mass yield of organic aerosols, ΔMTA(t) is the amount (g×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×L⁻¹). The fraction of each reactant in the aqueous phase was derived with Eq. (3).

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

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 m³ 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).

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.

2.74.1 Gas chromatography coupled with mass spectrometry

GC/MS analyses were performed ~~using~~with 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.~~

~~).~~ Precursors and products of ~~R1-3~~R3 were separated with a VF-WAXms column: ~~(Agilent, 30 m × 0.25 mm × 0.5 μm)~~ and quantified in the EI mode. The column ~~head pressure was set at 32.3 kPa, the total flow of the carrier gas (He) was maintained at 9.4 ml/min, the column~~ flow was 0.67 ml/min, ~~and (30 cm/sec).~~ the purge flow was 2 ml/min; ~~and the split-ratio~~linear velocity flow control mode was ~~set to 20~~used. 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 total analysis time was 22 min. The injection volume was 1 μl for all TAs, and the split ratio was set to 20.~~ The MS was operating in scan (m/z = 50-300) and SIM modes ~~(Table S9-S11).~~ Specific m/z values monitored in SIM mode are provided in Tables S1-S3.

~~Quantitative~~Qualitative analyses were carried out in the NCI mode using methane and ammonia as reagent gases. In these analyses, a ZB-5MSplus column ~~(30m×Zebron, 30 m × 0.25 mm × 0.25 μm)~~ was used. The column ~~head pressure was 27.2 kPa, the total flow of the carrier gas (He) was 16.4 ml/min, the column~~ flow was 0.68 ml/min; ~~(30 cm/sec).~~ and the purge flow was 2 ml/min; ~~the injection volume was 0.5 μl in splitless. The linear velocity flow control mode was used.~~ 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 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 final linear increase at a rate of 15 °C/min to 250°C, with a 1 min hold. ~~The~~The analysis time was 32.58 min. The injection volume was 0.5 μl (splitless mode), and the MS operated in the scan mode (m/z = 50-300).

2.74.2 Liquid chromatography coupled with time-of-flight mass spectrometry

~~Analyses~~LC-ESI/ToF/MS analyses were carried out with a Waters ACQUITY UHPLC liquid chromatograph coupled with the Xevo G2 ToF/MS instrument equipped with an ESI source operating in the negative ionization mode. The ESI source conditions were: source temperature 100°C, offset 80V, ~~desolvation~~Desolvation temperature 350°C, capillary voltage: 2.8kV, sampling cone: 40V, ~~cone~~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 a 0.2% formic acid solution in water (pH ≈ 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: initially 5%B for 5 min, then a linear increase to 45%B over 15 min, then a linear increase to 95% B over 2 min, kept for 2 min, then a decrease to 5% B over 1 min, kept for 2 min; ~~total~~Total runtime was 27 min. Elemental compositions were assigned to the detected TACs, assuming they were singly charged, deprotonated pseudo-molecular ions [M-H]⁻ composed of C, H, and O atoms.

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2.5 Product identification and quantitative analyses

Products were analyzed with GC-EI/MS, GC-NCI/MS, and LC-ESI/ToF/MS (section 2.4). Most structural assignments were based on MS data, including molecular masses, fragmentation patterns, elemental compositions, and plausible formation mechanisms of the detected products. Only TAs under investigation: FCH, BNL, MTH, menthone, fenchone, and camphor (Fig. 1), and camphoric acid were quantified with authentic standards. At the same time, the majority of non-acidic products were quantified with GC-EI/MS using 2-hydroxy-3-pinaneone, camphorquinone, and camphanediol as surrogate standards (Tables S1-S3), which were assigned to specific products with similar structural motifs and close retention times. Calibration of the GC-EI/MS instrument was performed in the concentration range from 0.04 to 0.4 $\mu\text{g L}^{-1}$. Linear coefficients of determination for all quantified analytes were >0.99 (Tables S1-S3). For some products generated in low quantities, particularly TACs, lacking experimental data on temporal evolution, their yields were derived from the kinetic model (section 2.7).

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

$$[\text{Product}]_t = \text{Yield} \times \Delta[\text{TA}]_t \quad (1)$$

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

2.6 Structure-activity relationship

The structure-activity relationship (SAR) was used to predict the $k_{\text{OH}_{\text{aq}}}$ values (Witkowski et al., 2024). In SARs based on Atkinson's group contributions approach (Monod and Doussin, 2008; Kwok and Atkinson, 1995), the bimolecular reaction rate coefficient $k_{\text{OH}_{\text{aq}}}$ ($\text{M}^{-1}\text{s}^{-1}$) for a given molecule is derived as a sum of site-specific values – Fig. 2.

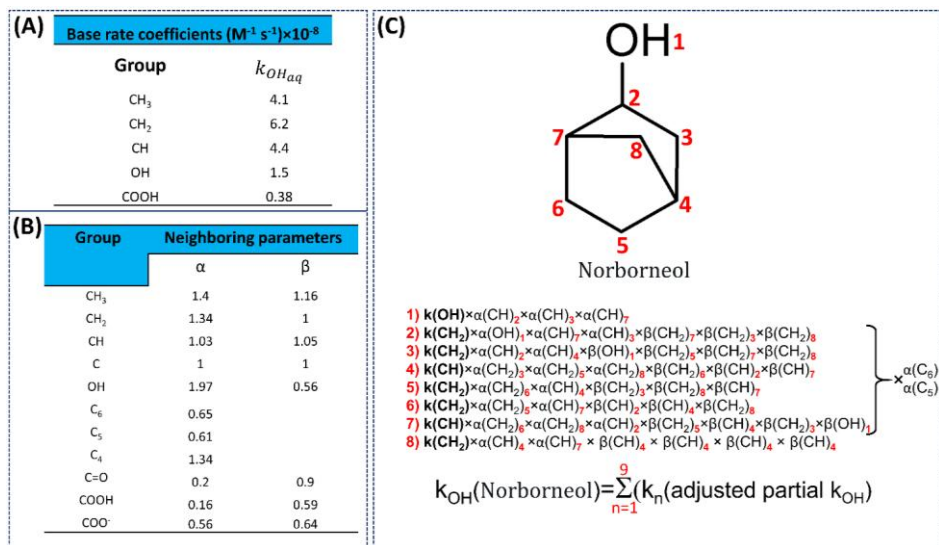


Figure 2: Structure-activity relationship parameters: base rate coefficients (A), neighbouring factors (B), and (C) an example of deriving partial and total $k_{OH_{aq}}$ values for norborneol. (B) values of neighboring factors >1 correspond to activation, whereas values <1 indicate a deactivating effect.

The SAR model utilized the base $k_{OH_{aq}}$ values (Fig. 2A) for groups with abstractable H—atoms, which are modified via α and β neighbouring parameters (Fig. 2B) of the adjacent moieties. Note that norborneol (Fig. 2C), the same as FCH, BNL (Fig. 1), contains fused C₅ and C₆ rings. Hence, all base $k_{OH_{aq}}$ values for CH₃ groups in positions 2-7 (Fig. 2C) are modified by the C₅ and C₆ α and β neighboring factors (Fig. 2B). Afterward, the adjusted $k_{OH_{aq}}$ are added to yield a total value – Fig. 2C. Here, SAR was used to derive total and partial $k_{OH_{aq}}$ values for the observed products of reactions R1–R3, which are provided in Tables S4-S6.

2.7 Kinetic modeling

Kinetic modeling was performed using the Acuchem program (Java version) (Braun and Herron and Kahaner, 1988). Kinetic models of R1–R3 were developed using the observed temporal evolution of the reactants, their formation yields, and reaction pathways proposed based on structural assignments, SAR results, and mechanistic implications. The reactions in the models include H₂O₂ photolysis (reactions 1–5 in Tables S7–S9) and the formation and interconversion reactions of tentatively identified products. Most of the $k_{OH_{aq}}$ values used in the kinetic models were predicted with SAR; measured values were available only for FCH, BNL, MTH, and camphoric acid (Witkowski et al., 2024; Otto and Schaefer and Herrmann, 2018).

Initially, the models were adjusted by fitting the simulated temporal evolution of major (non-acidic) products to the experimental data. To this end, the yields of non-acidic products, quantified using surrogate standards, were adjusted, while the yields of primary ketones, quantified using authentic standards, were kept unchanged. This approach was adopted due to additional uncertainty arising from differences in GC-EI/MS response factors between the surrogate standards and target compounds (Bergmann et al., 2018). After adjusting the model, the yields of products formed in low quantities, particularly TACs, were derived using Eq. (1) from their simulated temporal evolution and were subsequently adjusted based on relative signal intensities from the LC-ESI/ToF/MS measurements.

2.8 Yields of aqueous secondary aerosols

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 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 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 L⁻¹). The fraction of each reactant in the aqueous phase was derived with Eq. (3).

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

In Eq. (3), $\%_{aq}$ is the fraction of each reactant in the aqueous phase. It depends on LWC and is calculated by multiplying the dimensionless Henry's law constant, H^{cc} , by the volume of water in 1 m³ of air. Experimentally measured values were used whenever available, but the majority of H^{cc} values (Tables S10—S12) used in the models were predicted using HenryWin v4.11 (Episuite4.11).

2.9 Control experiments and uncertainty analysis

Control measurements performed without adding H₂O₂ to the reaction solution confirmed that the ~~MTAs~~TAs under investigation (Fig. 4) were not photolyzed with the UVB radiation used to generate OH (section 2.2). Also, no “dark” reactions (within the timescale of the experiments) interactions were observed between the precursors and H₂O₂ while the within the timescale of the experiments when the reactor lamps were kept off. All measurements were carried out at least three times. The uncertainty associated with the use of authentic standards was derived as 2σ values from triplicate experiments and usually did not exceed 10%. At the same time, the use of surrogate standards introduces a significantly higher uncertainty. However, because the yields initially obtained using surrogate standards were further adjusted based on experimental data, a 30% uncertainty was imposed on all product yields lacking authentic standards; this value was increased to 50% for the yields derived only from kinetic models (section 2.7).

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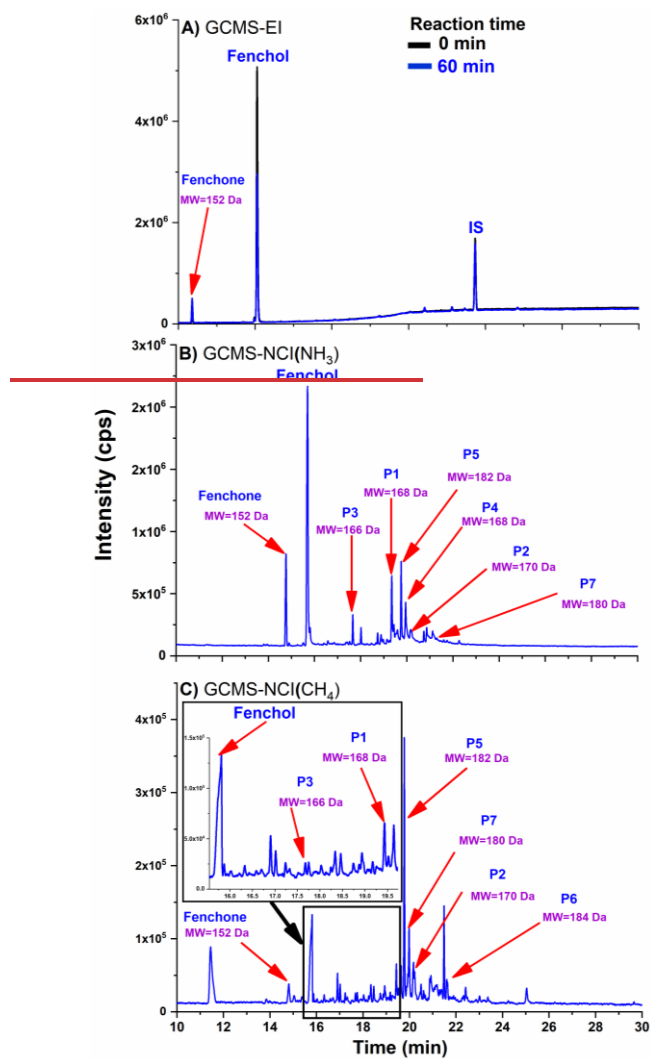
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3 Results and discussion

3.1 Mechanism/Analysis of OH reaction with fenchol

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

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395 The acquired chromatographic and mass spectrometric data were then used to propose the structures and formation pathways of the detected products, as detailed in sections 2.5 and 2.7. Products of R1—R3 were analyzed with GC/MS-EI, GC/MS-NCI

(section 2.4.1), and LC-ESI/ToF/MS (section 2.4.2). In addition to qualitative data, some products were quantified with GC/MS-EI (Tables S1-S3). At the same time, molecular masses of products of R1—R3, and further structural characteristics, were obtained from GC/MS-NCI measurements, due to a much lower degree of fragmentation in this ionization mode (Javelle and Righezza and Danger, 2021). GC/MS chromatograms of the products of R1 are presented in Fig. 3.

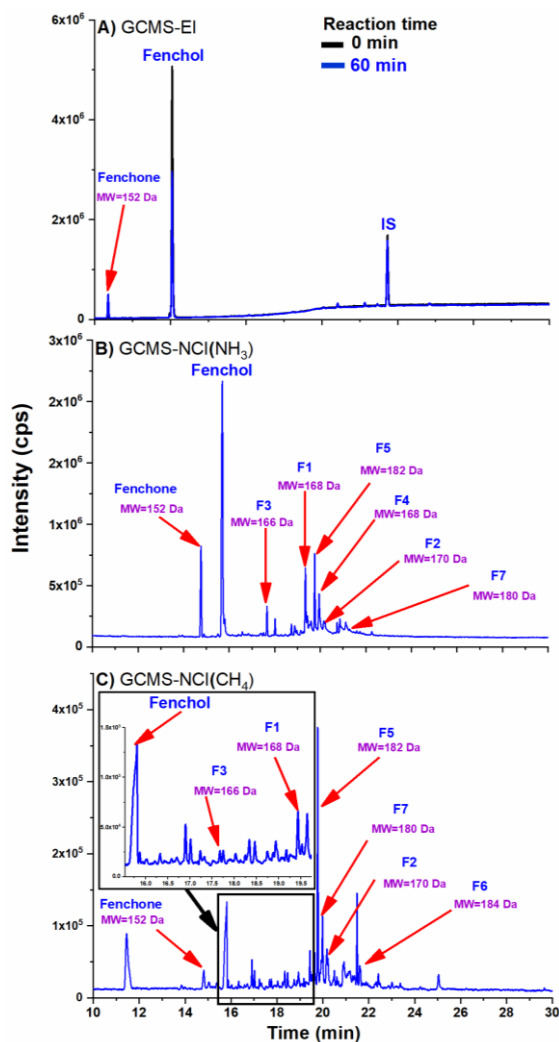
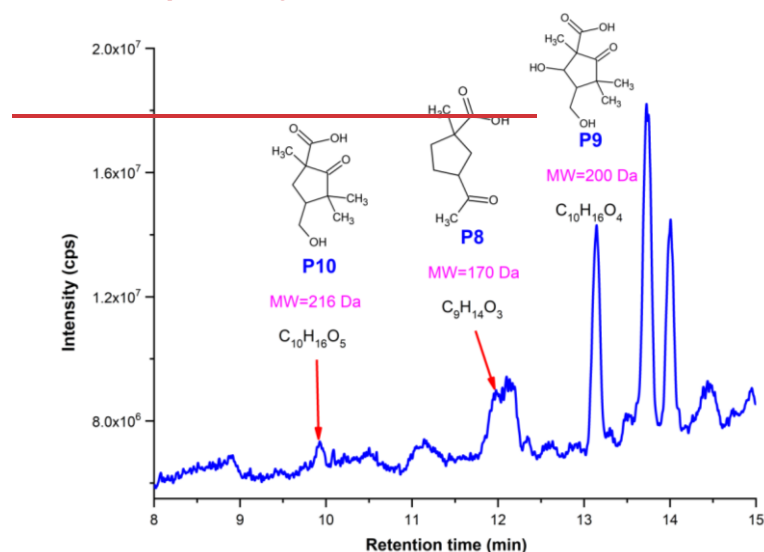


Figure 23: GC/MS chromatograms of the products of fenchol (FCH) + OH reaction (R1) detected with EI (A) and; NCI using NH₃ (B), and CH₄ (C) as reagent gases. Note that different chromatographic columns were used for GC-EI/MS and GC-NCI/MS analyses (section 2.74.1), resulting in different retention times between chromatograms acquired using different ionization modes.

In the EI mode, only the formation of fenchone from R1 was observed (Fig. 2A). ~~Additional~~ Many additional products were detected with NCI, (Fig. 3B and C), due to the higher overall sensitivity for products P1-P7F1-F7 in the NCI mode (Fig. 2B and C) (Javelle and Righezza and Danger, 2021) (Javelle and Righezza and Danger, 2021). Similar Very similar results were obtained for both reagent gases, but the sensitivity was significantly about 10-times higher for NH₃. For this reason, neutral non-acidic products of R1—R3 were identified based on the data obtained for analyzed with NCI using NH₃ as a reagent gas. All GC/MS chromatograms for R2 and R3 are shown in Figs. S1 and S2. Moreover, the results of LC-ToF/MS analyses confirmed was used to study the formation of TACs from— results for R1—are presented in Fig. 3—4, and data for R2 and R3 are provided in Figs. S3 and S4.



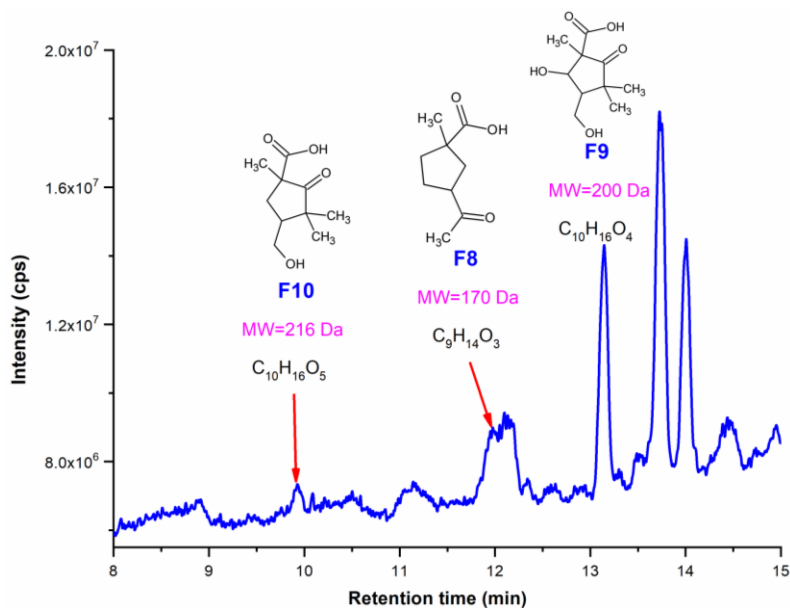


Figure 34: LC-ToF/MS chromatogram of TACs formed from OH reaction with fenchol – R1.

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

3.2 Mechanism of aqueous OH reactions with terpenoid alcohols

Aliphatic WSOCs, including TAs and products of R1–R3 (Fig. 1), react with OH via alkyl H-atom abstraction, with a minor contribution of acidic H-atom abstraction and single-electron transfer (SET) reaction for carboxylic acids and carboxylate anions, respectively (Witkowski et al., 2021; Ervens and Gligorovski and Herrmann, 2003). Therefore, the intramolecular selectivity of OH in R1–R3 was analyzed with SAR (section 2.6), by deriving the partial $k_{OH_{aq}}$ values, which identified contributions of individual H-atom abstraction sites to the total $k_{OH_{aq}}$ value – Fig. 5.

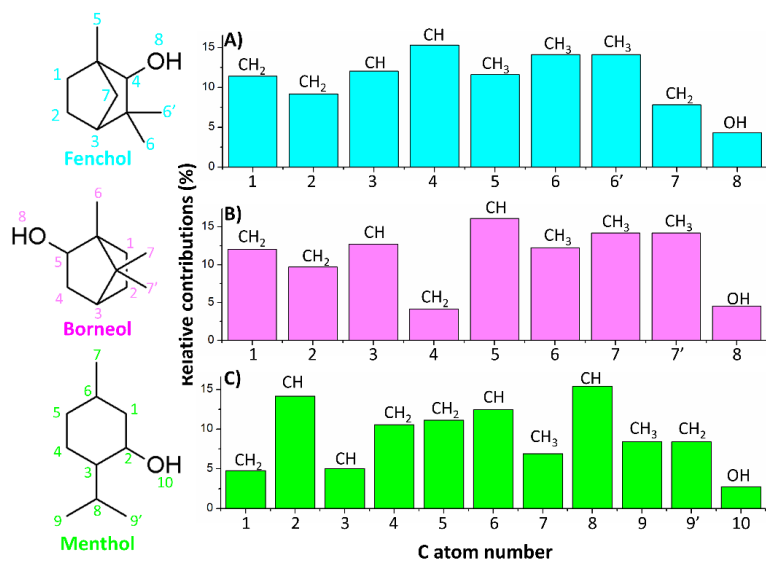


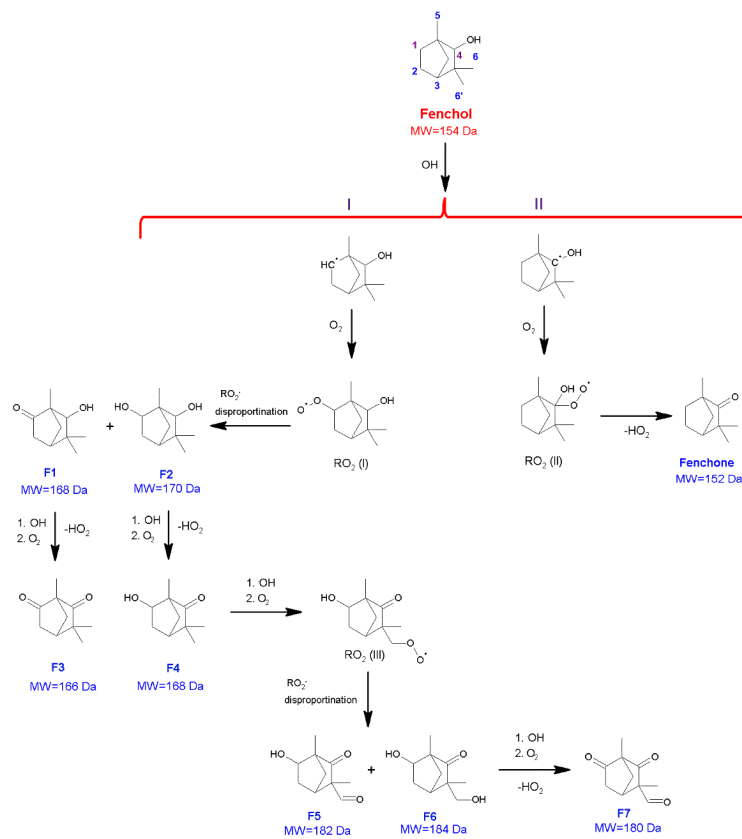
Figure 5: The relative values of partial rate coefficients for the aliphatic H-atom abstraction from fenchol (A), borneol (B), and menthol (C) predicted with SAR (section 2.6). SAR results for all reactants are provided in Tables S4-S6.

For all reactants, the predicted intramolecular selectivity of OH was strongly influenced by oxygen-containing moieties, as well as C₅ and C₆ rings, which generally exhibit stronger activating and deactivating effects in SAR than CH_x groups (Fig. 2). The SAR model used predicted that for all TAs, the majority of partial $k_{OH_{aq}}$ values (Fig. 5) were of the same order. Unlike in the gas phase, in aqueous solutions OH exhibits little preference for H-atom abstraction from higher-order CH_x groups (Rudakov and Volkova and Tretyakov, 1981). This phenomenon has been attributed to steric effects and solute-solvent interactions (Monod and Doussin, 2008; Kopinke and Georgi, 2017; Rudakov and Volkova and Tretyakov, 1981). In water, OH is strongly hydrated, which greatly increases its effective size, making site-specific reactivity depend more on steric hindrance (Monod and Doussin, 2008). Also, WSOCs and OH are trapped inside the water cage, which increases their contact

time (Kopinke and Georgi, 2017). Consequently, because reactants can reorient inside the water cage (Kopinke and Georgi, 2017), the selectivity of OH towards different CH₃ groups is more uniformly distributed (Monod and Doussin, 2008; Rudakov and Volkova and Tretyakov, 1981). For these reasons, the predicted intramolecular selectivity of OH in aqueous reactions depends primarily on the local molecular environment and not on carbon order, as reflected by the values of base $k_{OH_{aq}}$ (Fig. 2A) and neighbouring factors (Fig. 2B) in aqueous SARs (Monod and Doussin, 2008; Witkowski et al., 2024). Reaction pathways proposed for R1—R3 were based on SAR results and experimental data and involved known reactions of alkoxy (RO) and peroxy (RO₂) radicals (Russell, 1957; Bennett and Summers, 1974). Because partial $k_{OH_{aq}}$ derived with SAR represent the relative contributions of the H-atom abstraction site, their values provide information on reaction pathways and thus distribution of products (Mellouki and Le Bras and Sidebottom, 2003; Minakata and Von Gunten, 2023). At the same time, because relatively similar partial $k_{OH_{aq}}$ values were obtained for most alkyl H—atoms in TAs under investigation (Fig. 5), strongly indicating the formation of many isomeric products, all possible pathways are not discussed in sections 3.2.1-3.2.3 for clarity. Furthermore, the formation of TACs from R1—R3 was based primarily on mechanistic implications, as generating the —COOH moiety requires specific pathways. Moreover, in the proposed mechanisms, OH does not attack tertiary C—atoms because tertiary alkyl radicals are not readily converted into stable products, particularly detected carbonyls, without fragmentation or rearrangement (Enami and Sakamoto, 2016). At the same time, the experimental data strongly indicated the formation of pairs of disproportionation products of RO₂ radicals (alcohol and carbonyl) from R1—R3 (Russell, 1957; Enami and Sakamoto, 2016), which retained the carbon skeleton of the precursors.

3.2.1 Mechanism of aqueous OH reaction with fenchol

Two pathways presented in Scheme 1 involve H—atom abstraction from position 1 (pathway I) and the formation of fenchone (pathway II).

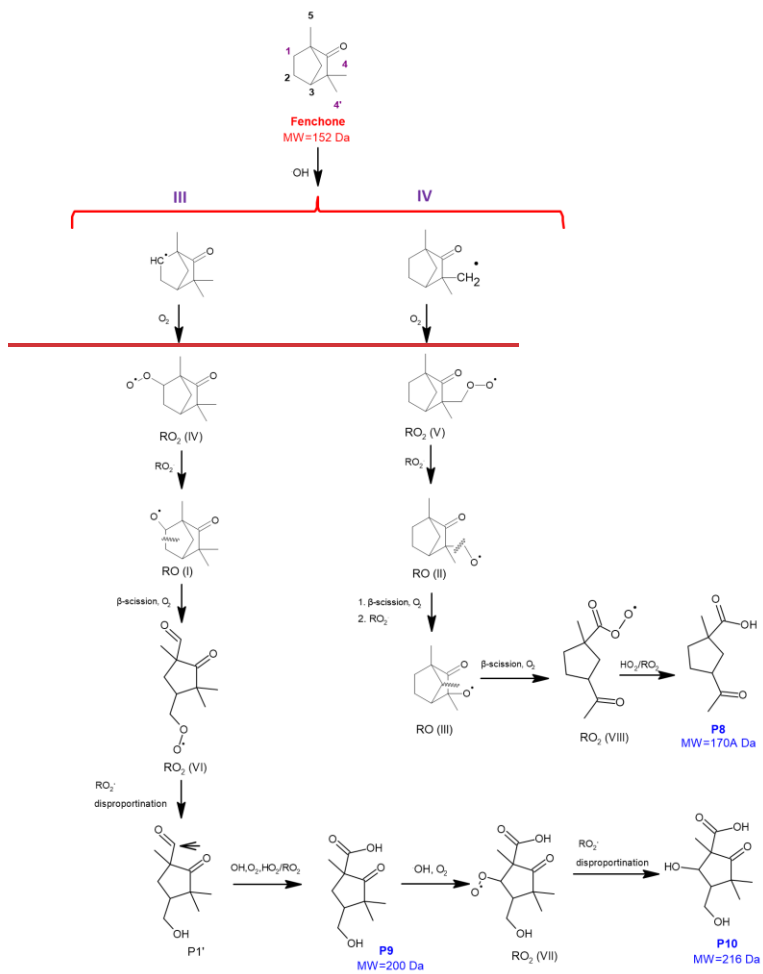


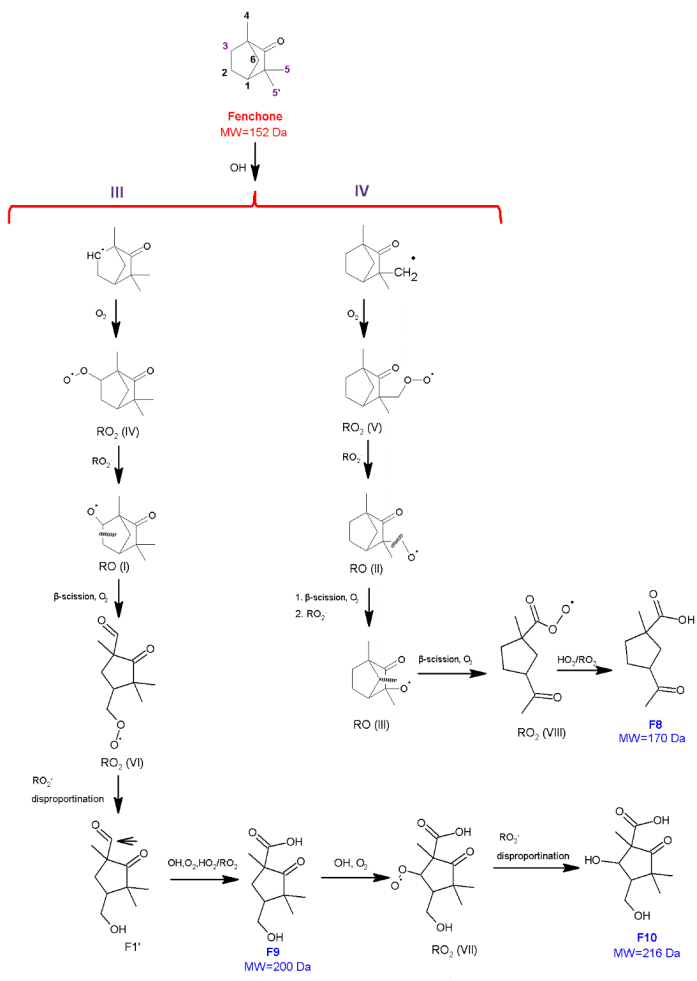
Scheme 1: Proposed mechanism of fenchol + OH reaction (R1). The products **detected-tentatively identified** in this work are highlighted in blue bold font. **The formation of all possible isomers-ispathways and isomeric products were not included for clarity.** The mechanism of R1 is continued in Scheme 2—oxidation of fenchone.

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In Scheme 1, pathway (I) yields peroxy radical $RO_2(I)$, which undergoes the Russell disproportionation reaction to produce carbonyl (P1) and alcohol (P2) products (Fig. 2) (Russell, 1957). Products P1 and P2 can further be converted to P3 and P4 following the conversion of $-OH$ to a carbonyl moiety, analogous to pathway II (Scheme 1). P3 exhibits lower predicted ($k_{OH_{avg}}=1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) than P4 ($k_{OH_{avg}}=2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Witkowski et al., 2024a). Consequently, P4 is oxidized faster than P3, yielding $RO_2(III)$, which then produces a carbonyl (P5) and an alcohol (P6) (Russell, 1957). Likewise, P6 ($k_{OH_{avg}}=2.8 \times 10^9$

480 $\text{M}^{-1}\text{s}^{-1}$) 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 HO_2 following the H-atom abstraction from the α -position of $-\text{OH}$
 (Denisov and Khudyakov, 1987; Puchkov and Buneeva and Perkel', 2005; Puchkov et al., 2013; Bradley et al., 2001).
 In Scheme 1, pathway (I) yields $\text{RO}_2(\text{I})$, which undergoes the disproportionation reaction to produce carbonyl (F1) and alcohol
 (F2) (Russell, 1957). Because SAR indicates that H—atoms in the α -position of the $-\text{OH}$ moiety are among the preferred
 485 abstraction sites (Table S4), the proposed mechanisms involve conversion of alcohols F1, F2, and also F7 into the
 corresponding carbonyls (Bradley et al., 2001; Puchkov and Buneeva and Perkel', 2005). According to SAR (Witkowski et
 al., 2024), the OH attack on the exocyclic CH_3 groups of F4 exhibited the highest partial $k_{OH_{aq}}$ values (Table S4) and the total
 $k_{OH_{aq}}$ value predicted for F4 ($2.8 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) was higher than that of F3 ($2.0 \times 10^9 \text{M}^{-1}\text{s}^{-1}$). Hence, F4 is proposed to react
 with OH to yield $\text{RO}_2(\text{III})$, which then produces another pair of disproportionation products - F5 and F6 (Russell, 1957).
 490 Likewise, in Scheme 1, F6 ($k_{OH_{aq}}=4.0 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) is oxidized faster than F5 ($k_{OH_{aq}}=2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$), resulting in F7,
 involving the H—atom abstraction from exocyclic CH_2 group (Table S4). In pathway II, FCH is converted to fenchone by
 elimination of HO_2 following the H—atom abstraction from the α -position of $-\text{OH}$ (Bradley et al., 2001; Puchkov and
 Buneeva and Perkel', 2005).
 Considering the well-known reactions of RO and RO_2 radicals, proposing a feasible mechanism for the formation of TACs
 495 detected with LC-ToF/MS (Fig. 34) directly from FCH is difficult. Consequently, in the proposed mechanism (Scheme 2),
 P8-P10, TACs F8-F10 are second-generation products of R1 formed/produced from the OH reaction with fenchone.





500 Scheme 2: Proposed mechanism for the OH reaction with fenchone. The products **Terpenoic acids** detected with LC-ToF/MS are highlighted in **bold blue bold font**.

In Scheme 2, RO₂(IV) and RO₂(V) are formed by the H-atom abstraction from the C1 and C4/4' positions of fenchone, respectively. Pathway III in Scheme 2 involves the formation of RO₂(IV), which then undergoes a β-scission reaction, resulting

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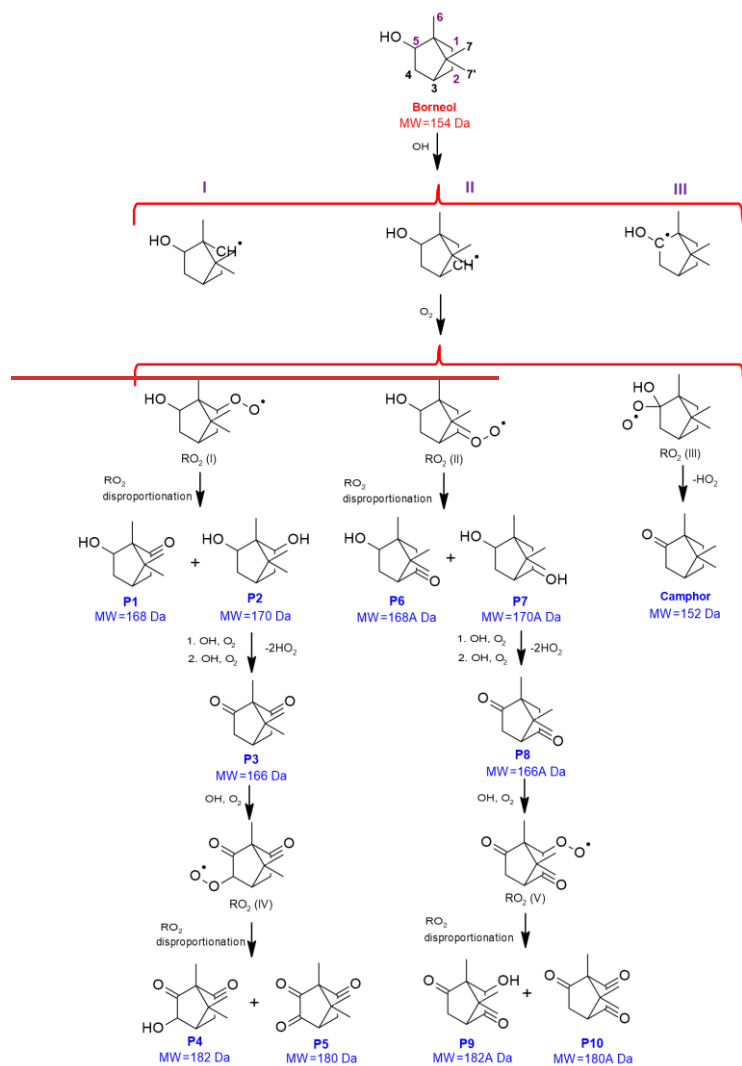
in $\text{RO}_2(\text{VI})$. $\text{RO}_2(\text{VI})$ yields by-product $\text{F1}'$, which is then likely rapidly oxidized to P9 following OH attack on the aldehyde moiety (Scheme 2) (Enami and Sakamoto, 2016a). Subsequently, P9 can undergo further oxidation to P10 via the addition of the —OH moiety to the cyclopentane ring. Pathway (IV) yields $\text{RO}_2(\text{V})$, which forms P8, following two consecutive β -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.

Partial $k_{\text{OH}aq}$ values estimated with SAR for fenchone were all very similar — Table S4, but the formation of TACs first required generating an aldehyde moiety via cyclohexane ring opening, which is then converted to —COOH acid following aldehydic H—atom abstraction (Enami and Sakamoto, 2016). In Scheme 2, $\text{RO}_2(\text{IV})$, and $\text{RO}_2(\text{V})$ are formed by the H—atom abstraction from the 3 and 5/5' positions of fenchone, respectively. Pathway III in Scheme 2 involves the formation of $\text{RO}_2(\text{IV})$, which then undergoes a β -scission reaction, resulting in $\text{RO}_2(\text{VI})$. $\text{RO}_2(\text{VI})$ yields by-product $\text{F1}'$, which is then likely rapidly oxidized to F9 following OH attack on the aldehyde moiety (Scheme 2) (Enami and Sakamoto, 2016). Subsequently, F9 can undergo further oxidation to F10, via the addition of —OH moiety to the cyclopentane ring. Pathway (IV) yields $\text{RO}_2(\text{V})$, which forms F8, following two consecutive β -scission reactions (Enami and Sakamoto, 2016).

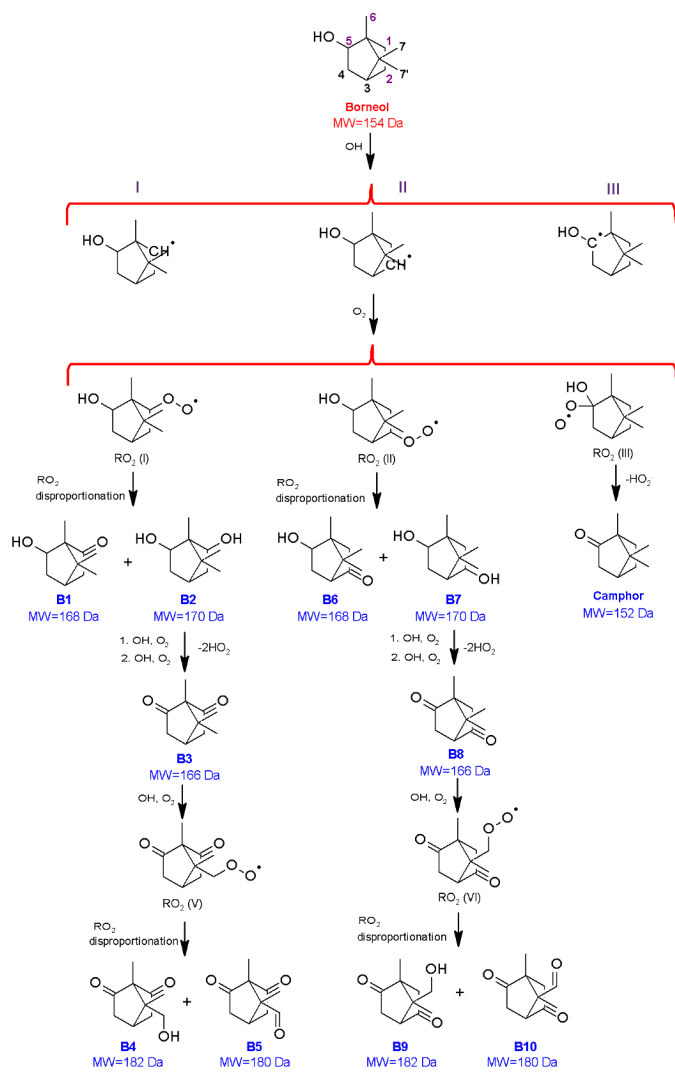
3.2.2 Mechanism of OH reaction with borneol

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.



The SAR results for BNL indicated that, of all H—atoms, abstraction from positions 4 and 8 (—OH group) was the slowest (Fig. 5B). Of the possible pathways of R2, reactions included in Scheme 3 involve the abstraction from C₆ ring positions 1 and 2 and position 5, resulting in the conversion of BNL into camphor.

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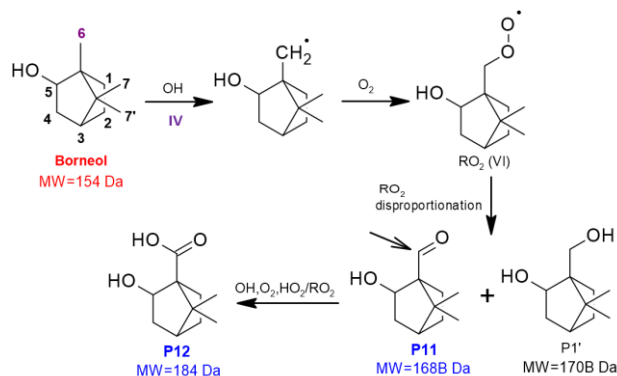


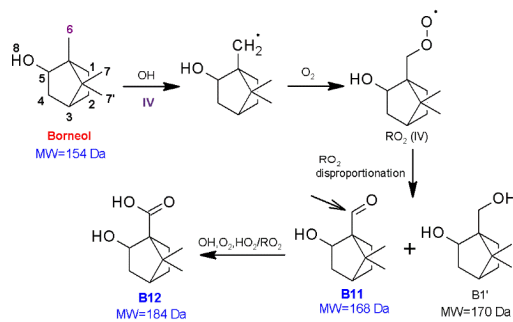
Scheme 3: Proposed mechanism of borneol (BNL) + OH reaction (R2). The detected products are highlighted in **bold blue bold font**. The formation of all possible isomers is not included for clarity. The mechanism of R2 is continued in Schemes 4 and 5 – formation of TACs.

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In Scheme 3, RO₂(I) and RO₂(II) are formed via pathways I and II, respectively. Formation of **P1-P2B1-B2** and **P6-P7B6-B7** can be explained via disproportionation reactions of RO₂(I) and RO₂(II) (Russell, 1957)(Russell, 1957). **Diols: P2** According to SAR, diols: **B2** ($k_{OH_{aq}}=3.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), **P7B7** ($k_{OH_{aq}}=3.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) are likely oxidized faster than **P1B1** ($k_{OH_{aq}}=2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and, **P6B6** ($k_{OH_{aq}}=2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Witkowski et al., 2024a),(Witkowski et al., 2024). For this reason, in Scheme 3, dicarbonyls **P3B3** and **P8B8** are formed by from B2 and B7. The results of SAR predictions (Table S5) also indicate that the H-atom abstraction by OH from the α -position of —OH moieties in **P2B2** and **P7**, followed by B7 was among the elimination of —HO₂ major reaction channels for these products. The conversion of BNL to camphor (pathway III in Scheme 3) likely occurs via the same an analogous mechanism (Denisov and Khudyakov, 1987; Puchkov and Buneeva and Perkel', 2005; Puchkov et al., 2013; Bradley et al., 2001)(Denisov and Khudyakov, 1987; Puchkov and Buneeva and Perkel', 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).

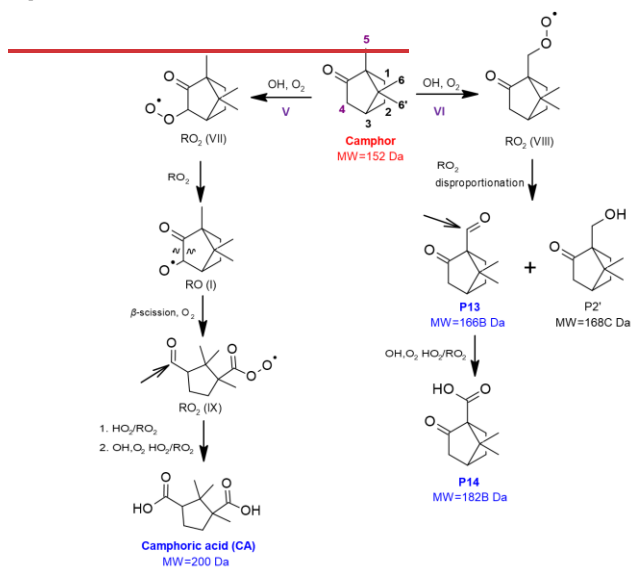
The Even though the formation of TACs (detected with LC/MS (see Fig. S3) from camphor was agains mechanistically more feasible, but likely, the acidic product **P12B12** may also be produced directly from the precursor BNL, involving the H-atom abstraction from the C6-position of BNL – Scheme 4.

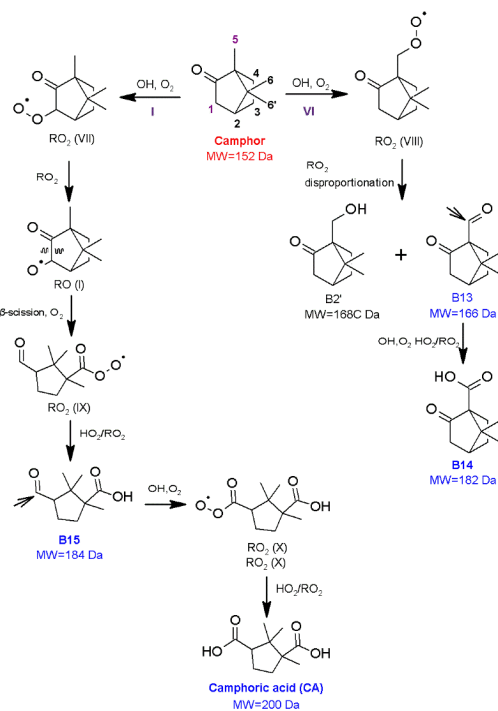




Scheme 4: Formation of P12B12 from OH reaction with borneol (R2) via pathway IV, involving the H-atom abstraction from the C6-position 6.

555 In Scheme 4, pathway (IV) yields $RO_2(VI)$, which undergoes the disproportionation reaction, resulting in P1' and P11, P14B1' and B1' and B11, the latter of which is further oxidized to P12B12 (Enami and Sakamoto, 2016b) (Enami and Sakamoto, 2016). The two by-products formed by pathway (IV) – P14B11 and P1'B1' – were not detected, likely due to their low formation yields and rapid conversion of P14B11 to P12B12. Camphoric acid and P14B14, 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 **P14B14) are highlighted in **bold blue bold font**.**

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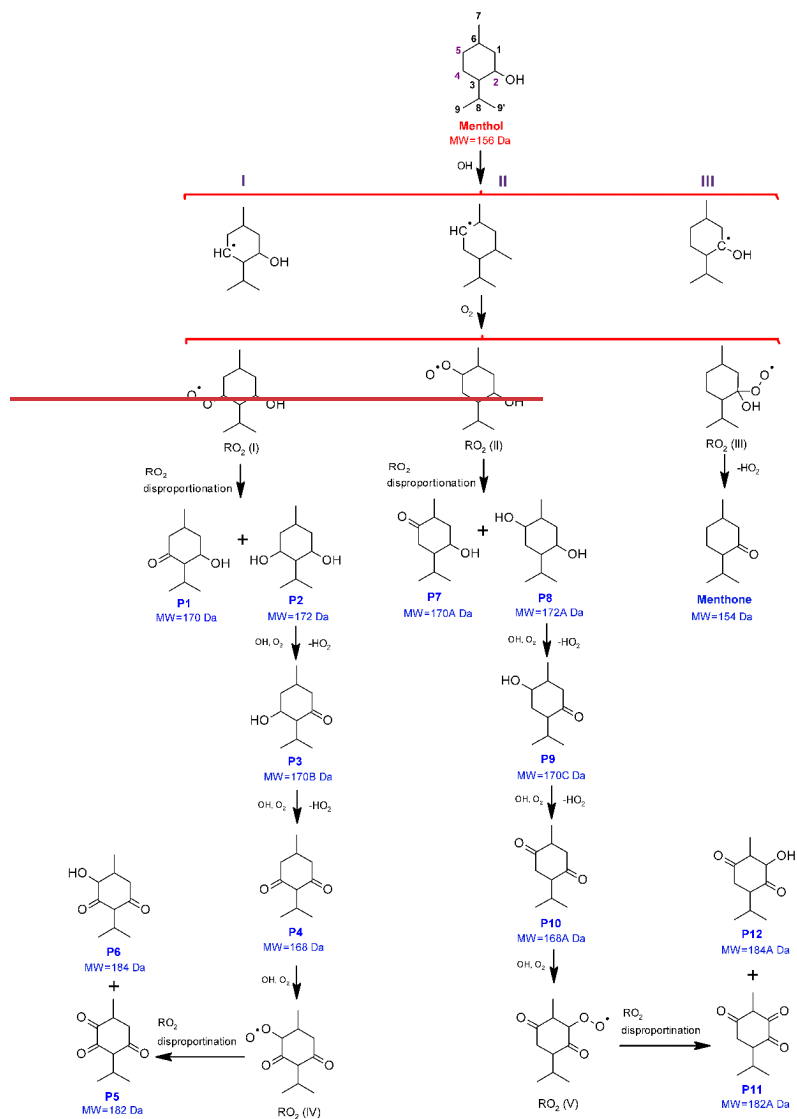
Camphoric acid is formed via pathway V (Scheme 5), which is analogous to pathway III in Scheme 2, and P14 is produced via pathway (VI), analogously to pathway IV in Scheme 4 (Enami and Sakamoto, 2016b).

In camphor, H—atom abstraction from position 1 leads to B15, which is oxidized to camphoric acid following aldehydic H—atom abstraction (Enami and Sakamoto, 2016). According to SAR (Table S5), position 1 in camphor is the least preferred H—atom abstraction site in camphor, but it leads to camphoric acid, which is formed following aldehydic H—atom abstraction from B15. The formation of B14 (pathway IV in Scheme 5) proceeds by the same mechanism (Enami and Sakamoto, 2016).

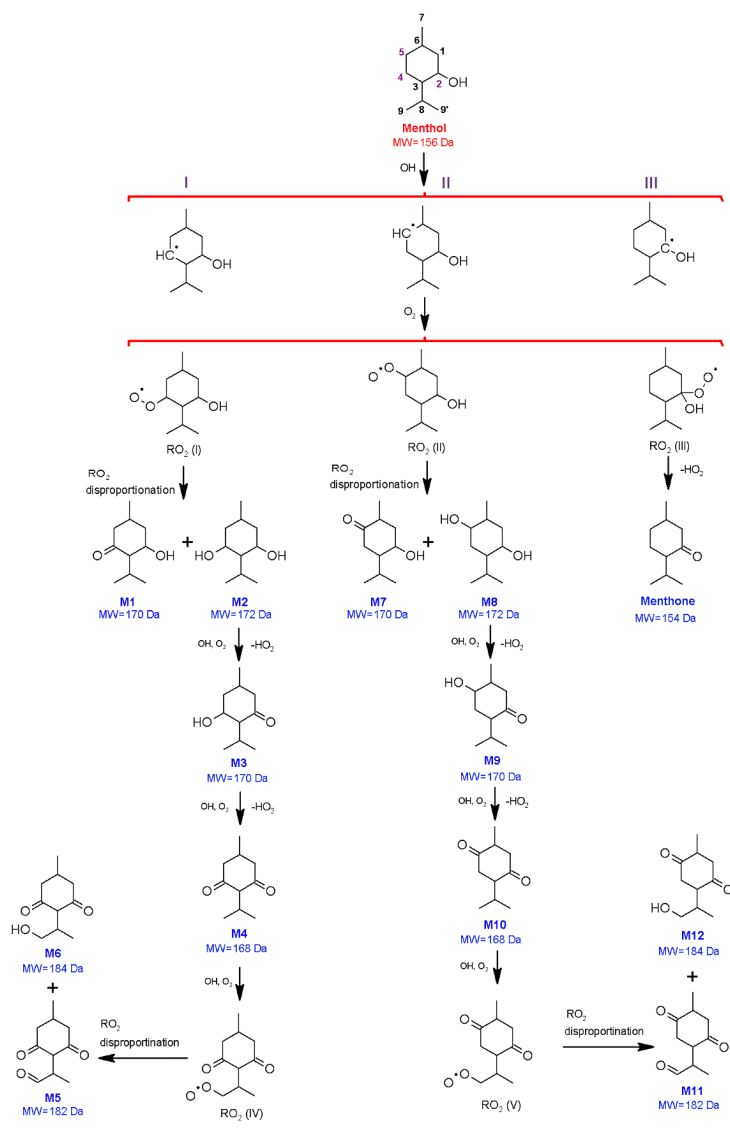
3.2.3 Mechanism of OH reaction with menthol

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.

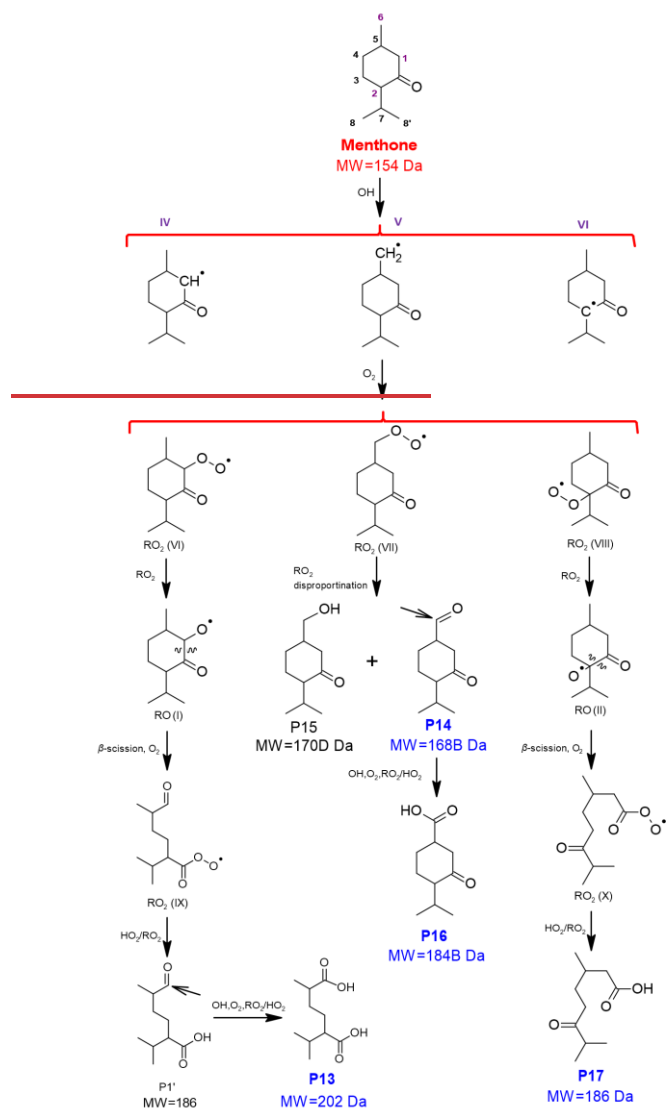


In MTH, according to SAR predictions (Fig. 5C), positions 1, 3 were the least preferred H—atom abstraction sites, followed by positions 7 and 10 (alcoholic H—atom), whereas the rest of the partial $k_{OH_{aq}}$ values were relatively similar. The possible pathways of R3 in Scheme 6 involve H-atom abstraction from positions 2 (conversion into menthone), 4, and 5.

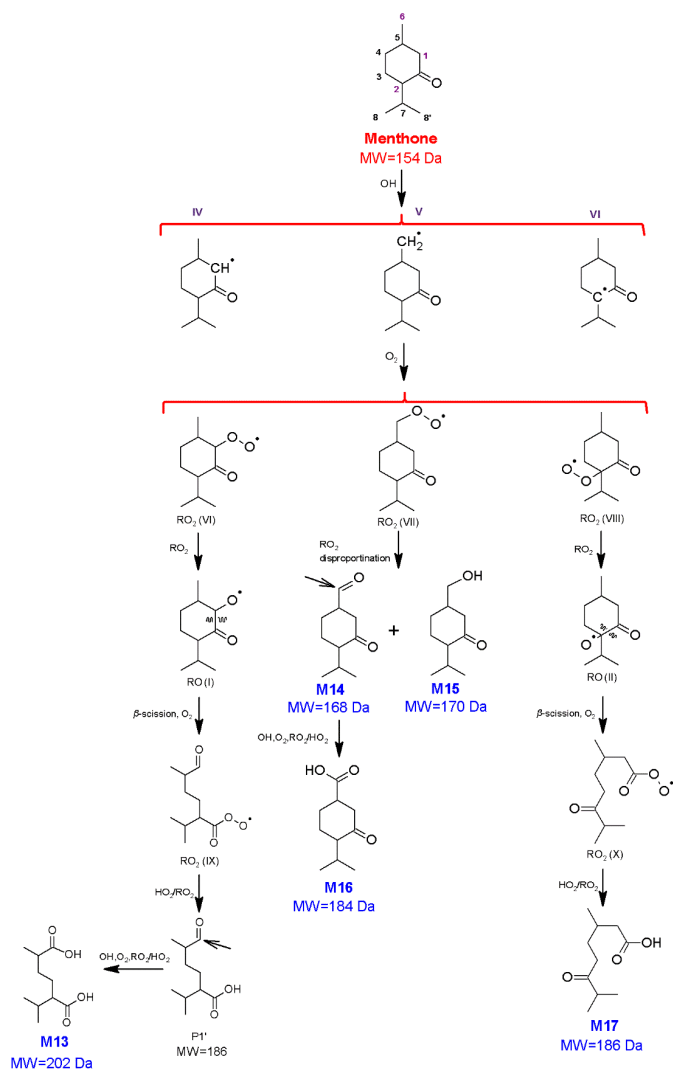


Scheme 6: Proposed mechanism of menthol (MTH) + OH reaction (R3). Products observed in this work are highlighted in bold blue bold font. The formation of all possible isomers is not included for clarity. The mechanism of R3 is continued in Scheme 7 – oxidation of menthone.

In Scheme 6, RO₂(I) and RO₂(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 ($k_{OH_{MTH}}=6.1\times10^9\text{-M}^{-1}\text{s}^{-1}$), and P8, ($k_{OH_{MTH}}=5.7\times10^9\text{-M}^{-1}\text{s}^{-1}$), which likely react faster than P1 ($k_{OH_{MTH}}=4.3\times10^9\text{-M}^{-1}\text{s}^{-1}$) and P7 ($k_{OH_{MTH}}=4.1\times10^9\text{-M}^{-1}\text{s}^{-1}$), respectively—Scheme 6 (Witkowski et al., 2024a). In pathways I and II, the elimination of HO₂ 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.



595 In Scheme 6, RO₂(I), and RO₂(II) are formed via pathways I and II, respectively, and undergo the disproportionation reaction,
leading to pairs of isomeric products: M1, M7, and M2, M8. Afterward, M3 and M9 are formed in Scheme 6 by oxidation of
M2 ($k_{OH_{aq}}=6.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), and M8 ($k_{OH_{aq}}=5.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), which likely react faster than M1 ($k_{OH_{aq}}=4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$)
and M7 ($k_{OH_{aq}}=4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), respectively (Witkowski et al., 2024). In pathways I and II, the elimination of HO₂ from M3
and M9 results in M4 and M10, respectively (Bradley et al., 2001; Puchkov and Buneeva and Perkel', 2005). Further oxidation
600 of M4 and M10 results in M5, M6, and M11, M12, which are formed by the disproportionation reactions of the corresponding
RO₂ radicals (Russell, 1957). The formation of menthone via pathway III in Scheme 6 involves the H-atom abstraction from
position 2, followed by elimination of HO₂ (Bradley et al., 2001; Puchkov and Buneeva and Perkel', 2005). TACs formed from
R3 (Fig. S4) are most likely produced from menthone – Scheme 7.



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

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 RO₂ radicals. Afterward, RO₂ (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-In menthone, H-atom abstraction from positions 2, 3, and 6, resulting in aldehyde by-products, is characterized by the lowest partial $k_{OH_{aq}}$ values (Table S6). Pathways IV-VI in Scheme 7 involve the formation of M13, M16, and M17 following menthone C_6 ring opening via the β -scission reaction and disproportionation of resulting RO_2 radicals (Enami and Sakamoto, 2016). Subsequently, the aldehyde by-products are converted to TACs following aldehydic H-atom abstraction (Enami and Sakamoto, 2016)

3.3 Product yields and comparison with the gas-phase data

Molar yields derived with Eq. 1 (section 2.5) indicated that >88% of the R1—R3 products (Table 1) were quantified using the experimental approach used in this work—Fig. S1. At the same time, even though near-carbon balance is obtained, the quantitative data are subject to a large uncertainty (see section 2.9). For all precursors/TAs under investigation, the major products were neutral/non-acidic molecules containing —OH and C=O moieties, and the yields of TACs were between/ranged from 1 and to 5% – Table. 1.

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

Precursor	Molar Product yields			
	Neutrals ^a	Non-acidic ^a	Acids ^b	Total ^c
Fenchol	0.91±0.07	0.27	0.03±0.02	0.94±0.07
Borneol	0.95±0.10	0.27	0.05±0.02	0.99±0.10
Menthol	0.87±0.05	0.26	0.01±0.005	0.88±0.05

▲ Measured with authentic or surrogate standards ▲ Values obtained from the kinetic models ▲ Uncertainties derived from the experimental uncertainties of the

The yields of individual TACs from R1-R3 obtained in this work are comparable with the data obtained for OH reaction with terpenoid acids and diols in the gas (Müller et al., 2012) and aqueous phase (Aljawhary et al., 2016; Jain et al., 2024). Moreover, the yields of some non-acidic products in Table S16 are high, reaching up to 22% for R1 and 15 and 19% for R2 and R3, respectively. Because all possible reaction pathways were not discussed for clarity (section 3.2), mechanisms of R1—R3 likely

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involve formation of many isomeric products, which are only partially resolved by GC/MS. For this reason, the carbon mass is very likely more uniformly distributed among the isomeric products of R1—R3. 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 CH₃ 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.

Table 2. YieldsThe reactions of OH with MTH, FCH, BNL, and cyclohexanol were previously investigated in the gas phase (Ceacero-Vega et al., 2012). For instance, formation of fenchone and products F5–F7 from R1 and B1, B2, B6, and B7 from R2 was observed, likely occurring via similar mechanisms, but product yields in the gas phase were not reported (Ceacero-Vega et al., 2012). At the same time, the formation of TACs from R1—R3 was not previously reported, likely because low quantities of underivatized TACs are difficult to detect with GC/MS, which was previously used to study the product distribution from gas-phase oxidation of MTH, FCH, and BNL by OH (Ceacero-Vega et al., 2012). At the same time, the yields of the corresponding ketones from the OH reaction with FCH, BNL, and cyclohexanol in the gas phase were previously measured and were significantly higher than in the aqueous phase — Table 2.

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

Yield (%)			Reference
Alcohol	Ketone (product)	Aqueous phase ^a phase	Gas-phase
(precursor ^{precursor})			

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Fenchol	Fenchone	0.11±0.01	0.61±2.60.03	(Ceacero-Vega et al., 2012)(Ceacero-Vega et al., 2012)
Borneol	Camphor	0.12±0.02	0.49±1.0.01	(Ceacero-Vega et al., 2012)(Ceacero-Vega et al., 2012)
Menthol	Menthone	0.03±0.00003	-	
Cyclohexanol	CyclohexanoneCyclohexanone	-	0.55±0.606	(Bradley et al., 2001)(Bradley et al., 2001)

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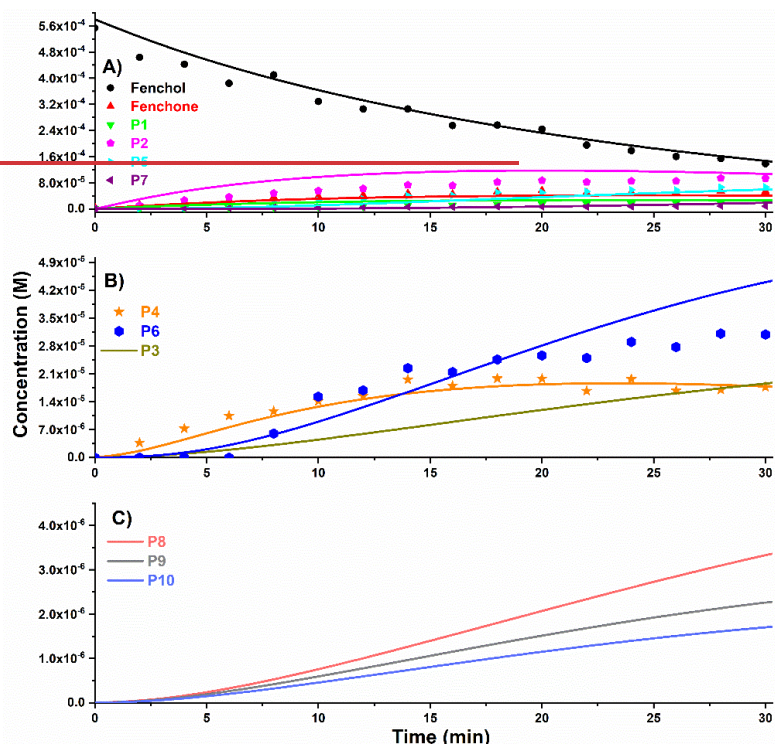
660 ^aMeasured with authentic standards
 In the gas phase, the measured yields of ketones from the reaction with OH with the cyclic alcohols were between 0.49 and 0.61—Table 2(Ceacero-Vega et al., 2012; Bradley et al., 2001). These data indicate that H-atom abstraction from the —OH moiety α -position was the main reaction pathway. This conclusion is also supported by the partial $k_{OH_{\text{eff}}}$ values estimated with the gas-phase SAR (Kwok and Atkinson, 1995; Ceacero-Vega et al., 2012).
 665 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 $k_{OH_{\text{eff}}}$ —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 (α -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).
 670 3.5 ^aMeasured with authentic standards
 In the gas phase, the measured yields of ketones from the reaction with OH with the cyclic alcohols (Table 2) are between 0.49 and 0.61 (Table 2). These data indicate that in the gas phase, H—atom abstraction from the —OH moiety at the α -position was the main reaction pathway for the cyclic alcohols listed in Table 2 (Bradley et al., 2001; Puchkov and Buneeva and Perkel', 2005). This conclusion is also supported by the partial $k_{OH_{\text{gas}}}$ values estimated with SAR (Ceacero-Vega et al., 2012),
 680 indicating that H-atom abstraction in the α -position of —OH is a major reaction channel (ca. 60%) for cyclic alcohols, consistent with the measured yields of corresponding ketones (Ceacero-Vega et al., 2012). At the same time, according to aqueous SAR, the abstraction of the H—atom adjacent to the —OH group contributes 5-15% to the total $k_{OH_{\text{aq}}}$. These SAR

predictions (Fig. 5) are consistent with the experimental data acquired in this work (Table 2), supporting differences in intramolecular selectivity of OH in reactions with TAs in the gas and aqueous phases, leading to lower yields of primary ketones from R1—R3, compared with the reactions in the gas phase.

3.4 Kinetic models

The kinetic models for R1–R3 are based on the measured product yields (Tables S8S16 and S9S17) and their proposed formation pathways (Schemes 1–7). For all precursors, even though the model was based on a simplified mechanism of R1—R3, a good agreement between with the experimental data was obtained; sample results obtained for R1 are. Measured and modelled temporal evolution of reactants in R1 is presented in Fig. 46, while data for R2 and R3 are provided in Figs. S6 and S7, respectively.

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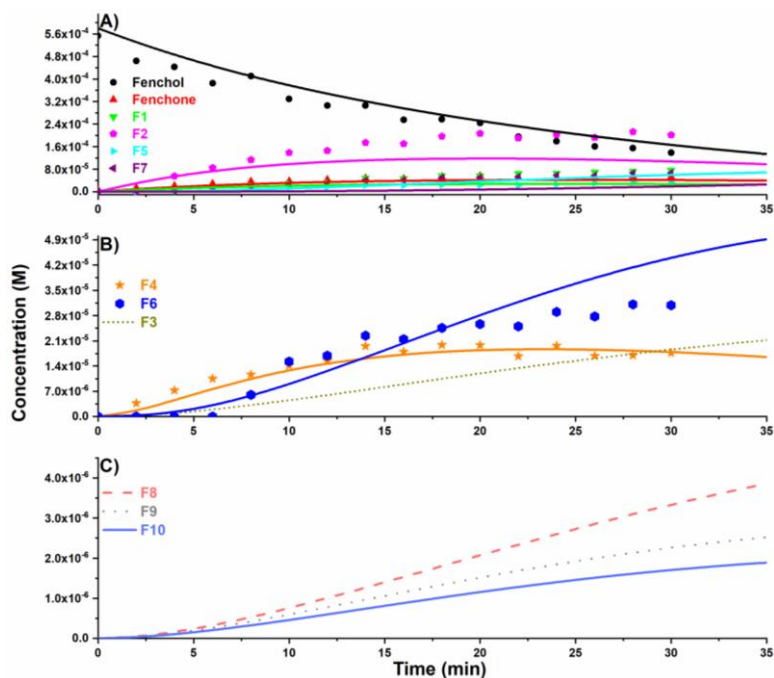


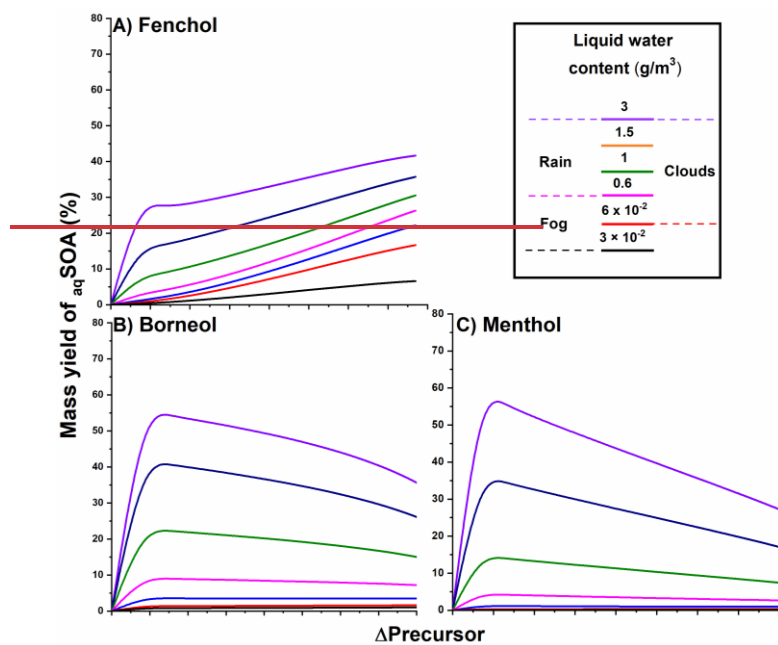
Figure 46: Measured and modeled temporal evolution of the reactants for the fenchol + OH reaction (R1). Points represent experimental data, and lines are the temporal profiles generated by the model. Structures of neutral/non-acidic (A and B) and acidic (C) products are shown in Schemes 1 and 2, respectively.

For R1, the box model accurately predicted/reproduced the temporal evolution of the reactants —with good accuracy (Fig. 4A, 6A and B) and was used to derive the yields of some products, particularly TACs (Fig. 6C). Only model data is shown for TACs and some neutral/non-acidic products since their yields were/could not be measured —(section 3.4). Very similar, satisfactory performance of the models was obtained (2.7). The predicted temporal evolution was combined with H^{cc} values for R2 and the reactants to estimate the yields of $_{aq}$ SOAs from R1—R3—Figs. S7 and S8.

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) (Witkowski et al., 2024). 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^{-14} M (remote clouds), ranged from 10 to 300 h (Bianco et al., 2020). The lower limit estimate is comparable with the 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 $[\text{OH}]_{\text{aq}} = 2.2 \times 10^{-12}$ M, which were on the order of minutes (Witkowski et al., 2024). Even though the three TAs under investigation have no documented emission sources from marine biota, reactions in marine clouds may still be relevant due to the (long-range) atmospheric transport and near the shoreline (Coggon et al., 2014). 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_2O_2 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 $[\text{OH}]_{\text{aq}}$ to μM level (Paulson et al., 2019), thereby shortening the lifetimes of semi-volatile TAs 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_2O_2 and organic hydroperoxides, Fenton and Fenton-like reactions, and ozonolysis of dissolved organic matter (Kuang et al., 2020a; Bianco et al., 2020). Such processes can increase cloud water $[\text{OH}]_{\text{aq}}$ to micromolar levels (Paulson et al., 2019), thereby shortening the lifetimes of semi-volatile TAs even by a few orders of magnitude. Consequently, the mass yields of aqSOAs (section 2.6) from R1- R3 were derived with Eq. 2 for LWC values ranging from 0.03 to 3 ($\text{g} \cdot \text{m}^{-3}$) - Fig. 57.



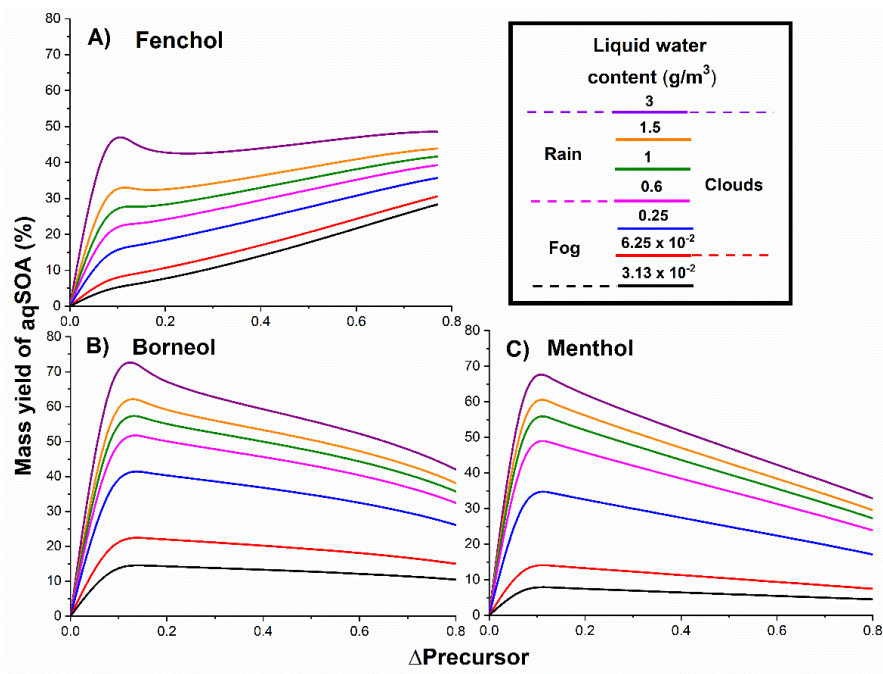


Figure 57: Modelled yields of aqSOA from fenchol (A), borneol (B), and menthol (C) as a function of LWC and reaction coordinate.

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

7. An increase in the yield of aqSOA for FCH (Fig. 5A7A) at the later stages of the reaction was observed, whereas BNL and MTH exhibited the opposite trend (Figs. 5B7B and C). The trends observed in Fig. 5B7B and C are due to the loss of the 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 S7Tables S8 and S9) are completely oxidized and thus removed by the time the precursors are consumed.

The yield of aqSOA from R3 (Fig. 5C7C) was somewhat lower than that of R2 (Fig. 5B7B). This couldcan 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 aqSOAs . For instance, in a study on the atmospheric degradation of cyclohexanol by OH, greater

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fragmentation of the precursor was observed, resulting in the formation of straight-chain alcohols and carbonyls (Bradley et al., 2001). In contrast, oxidation of precursors containing with bridged cyclohexaneC₆ rings yielded less fragmented oxidation products (Ceacero-Vega et al., 2012)(Ceacero-Vega et al., 2012).

The increase in $aqSOA$ in Fig. 5A7A is attributed to the significantly high H^{cc} values of the products of R1, particularly P5, P7, P9F5, F7, F9, and P40F10 (see Schemes 1 and 2 and Table S4S10). Additionally, the formation of highly oxygenated TACs (P9F9 and P40F10) from R1 also contributed to the increase in the predicted $aqSOA$ yield in Fig. 5A7A. Analogous products, with very high H^{cc} values, were not formed from R2 or R3 (Table S5, S6Tables S11 and S12).

The modelled yields of $aqSOA$ from R1-3 are between 10 and 70% (Fig. 5). In the gas phase, the yields of $gasSOA$ of $49.0 \pm 1.0\%$ 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 $aqSOA$ yields obtained here (Fig. 5). Hence, the formation of gas or aqueous SOAs from R1-3 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 Tg yr^{-1} (Guenther et al., 2012), comparable with the emission of 34 major MTDs of 14.9 Tg yr^{-1} (Guenther et al., 2012). Hence, the emission of FCH, BNL, and MTH can be roughly estimated at 1.5 Tg yr^{-1} , the global flux of $aqSOAs$ from R1-3 can be as high as 0.15 Tg 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 $aqSOAs$ 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.

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 vary greatly and appear to be structure-specific, e.g., lower values were reported for linear TAs (Lee et al., 2006).

The modelled yields of $aqSOA$ from R1-3 are between $10 \pm 3\%$ and $70 \pm 20\%$ (Fig. 7). In the gas phase, the yields of $gasSOA$ of $49.0 \pm 1.0\%$ for BNL and $60.9 \pm 2.6\%$ for FCH were reported (Ceacero-Vega et al., 2012), within the range of values obtained in this work. Moreover, the yields of $aqSOA$ for R1-3 are comparable with the values obtained for the aqueous OH reaction with terpenic acids (Aljawhary et al., 2016), diols (Jain et al., 2024) and green-leaf volatiles (Hansel et al., 2015; Richards-Henderson et al., 2014).

In estimating the $aqSOA$ flux, global and local scenarios are considered. As discussed in section 1, the global flux of all TAs was estimated at 15 Tg yr^{-1} (Griffin et al., 1999). Moreover, the average stratocumulus cloud coverage is 20%, and 15% of the lower troposphere is filled with clouds (Hoffmann et al., 2018; Prisle, 2021). Hence, taking into account the emissions of TAs (Tg yr^{-1}), availability of the aqueous reaction medium (15%), the aerosol yields estimated in this work (0.1-0.7) and their uncertainty ($\pm 30\%$), the global flux of $aqSOAs$ from the reactions of TAs with OH can be roughly constrained between 0.2 ± 0.1

and $1.5 \pm 0.5 \text{ Tg yr}^{-1}$. These values are comparable with the fluxes of aqSOA previously estimated for WSOC produced from OH-oxidation of α -pinene (1.3 Tg yr^{-1}) and limonene (0.15 Tg yr^{-1}) (Zaragoza et al., 2026), glyoxal and methylglyoxal ($2 - 23 \text{ Tg yr}^{-1}$) (Ervens, 2015). Hence, the estimated fluxes of aqSOA from TAs are significant when compared with the estimated flux of aqSOAs ($\sim 20\text{-}30 \text{ Tg yr}^{-1}$) from WSOCs derived from isoprene, monoterpenes and aromatics (Liu et al., 2012), but still much lower than the total flux of BSOAs estimated at $\sim 107 \text{ Tg yr}^{-1}$ (Hodzic et al., 2016; Kelly et al., 2018; Spracklen et al., 2011).

At the same time, emissions of BVOCs, including TAs and MTDs, vary strongly with vegetation type, phenological stage, and disturbance. For instance, among VOCs emitted by citrus trees, a TA (linalool) was the most abundant, exceeding the contribution from limonene and α -pinene by a factor of 10 and 20, respectively, with a 30-fold increase in emission during flowering (Gentner et al., 2014). Therefore, such episodic emissions can be regionally relevant, particularly during flowering, with some aromatic plants emitting terpene mixtures strongly enriched in oxygenated compounds. For example, oxygenated monoterpenes represented 62.3% of the leaf essential oil of *Tarchonanthus camphoratus*, with fenchol and α -terpineol accounting for 15.9% and 13.2%, respectively, compared with only 6.87% α -pinene and 1.18% limonene (Matasyoh et al., 2007). Although essential-oil composition cannot be equated directly with atmospheric flux, it identifies vegetation in which damage, harvesting, or heat-driven volatilization can produce emission mixtures enriched in TAs (Matasyoh et al., 2007). Field observations also indicate that emissions of oxygenated terpenoids coexist with rapid local oxidation. For instance, in the Landes pine forest, compounds consistent with linalool, linalool oxide, and camphor exhibited increased night time emissions, whereas more oxygenated secondary terpenoids peaked during the day (Li et al., 2020). These data indicate that aqueous processing of TAs may become particularly important in foggy or cloudy air masses passing over flowering plantations, aromatic vegetation, or recently disturbed canopies. Under such conditions, the combination of locally elevated precursor concentrations and higher LWC could contribute substantially to the local aqSOA flux.

5 Conclusions

This work provides a comprehensive mechanistic and quantitative investigation of aqueous OH ~~reaction~~ reactions with three representative ~~terpenoid monoalcohols—fenchol, borneol, and menthol~~ TAs—FCH, BNL, and MTH. The results obtained demonstrate that these semi-volatile oxygenated terpenoids ~~efficiently~~ undergo efficient aqueous oxidation, primarily yielding multifunctional, non-acidic products and smaller but atmospherically important fractions of low-volatility terpenoid 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 α -position of the hydroxyl group, highlighting the importance of solvation effects and different transition-state stabilization in both phases.

A key outcome of this study is the first quantitative estimation of aqSOA mass yields from terpenoid monoalcohols, reaching up to $\sim 70\%$ in air masses with high liquid water content. These yields are comparable with the previously reported gasSOA

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805 formation for ~~related precursors, indicating that the relative importance of aqueous versus gas-phase pathways is controlled by~~
~~the availability of liquid water~~ similar precursors and oxygenated organic gases. Moreover, ~~aq~~ SOA formation from TAs may
~~contribute to BSOA, particularly in regions with high MTD emissions.~~
Overall, the presented 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~~ provide a foundation for
810 improved representation of multiphase SOA formation in atmospheric models.

Data availability

Data can be obtained by contacting the corresponding author.

Author contributions

| B.W. designed the study and developed the methodology. P.J. and A.B. ~~optimized the methodology,~~ performed the
815 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 —

The authors declare that they have no conflicts of interest.

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