

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 likely contributes to the formation of secondary organic aerosol (SOA) from biogenic volatile organic compounds, but quantitative and mechanistic data for such precursors are limited. In this study, the aqueous-phase reactions of three atmospherically relevant terpenic 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 modelling. The objectives were to elucidate reaction mechanisms, identify major products, and quantify yields of aqueous SOA (_{aq}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 low-volatility terpenic acids formed as higher-generation products, providing new evidence for the formation of low-volatility compounds from aqueous OH reactions with TAs. The molar yields of quantified products approached unity within the estimated uncertainties, which were ca. 30%, primarily due to the use of surrogate standards. Based on these data, explicit kinetic box models were developed, successfully reproducing the measured temporal evolution of reactants. Modelled _{aq}SOA yields ranged from 10% to 70%, depending on liquid water content and reaction 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.

30 1 Introduction

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 $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) 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 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 $\sim 73.6 - 140 \text{ Tg yr}^{-1}$ (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).

In addition to isoprene and monoterpenes, oxygenated monoterpenoids (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 terpenoid 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).

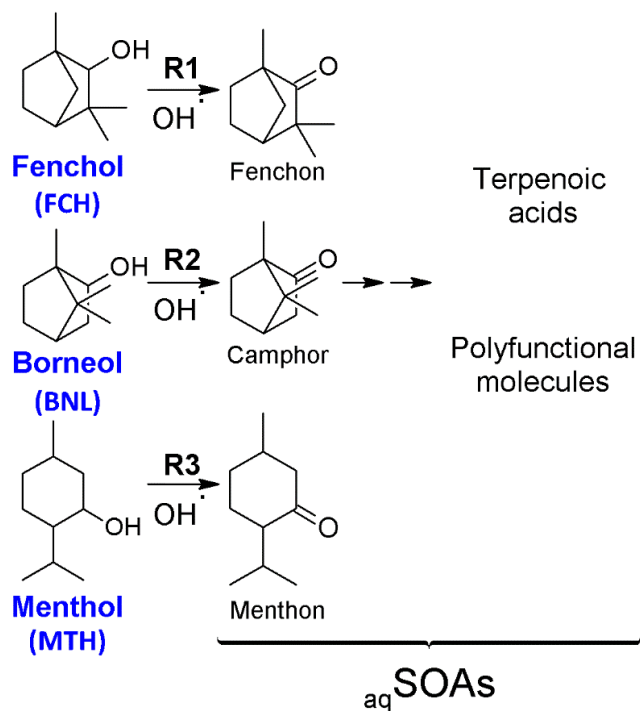


Figure 1: Precursors and reactions investigated.

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 *Tarhonanthus 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).

70 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
75 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
80 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
85 results in the formation of water-soluble organic compounds (WSOCs). The WSOCs contributing to monoterpenoic 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
90 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
95 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;
100 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
105 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 aqSOAs 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 aqSOAs 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
110 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
115 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
120 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 monoterpeneoic aqSOAs , 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
125 persist regarding the aqueous oxidation mechanisms and mass yields of aqSOA 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 aqSOA formation from the OH-initiated oxidation of MTDs, focusing on
130 reaction mechanisms and aerosol mass yields. An overarching goal was to constrain the global aqSOA flux from the aqueous
OH reactions with MTDs. As concluded in our previous study, in the atmosphere, FCH, BNL, and MTH can enter water-
containing particles considering their dimensionless Henry’s law constants ($H^{\text{cc}} \approx 1 \times 10^3$) (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 (Witkowski et al., 2024). Hence, these TAs were studied in this
135 work as potential precursors of aqSOAs .

The TAs shown in Fig. 1 share structural features with many MTDs and atmospherically abundant monoterpenes, namely
alkyl-substituted C_6 rings, fused with C_5 rings (Jenkin, 2004; Kamens and Jaoui, 2001; Khalaj et al., 2025). The TAs under

investigation ($C_{10}H_{18}O$) are also suitable representative precursors for studying the formation of $_{aq}SOAs$ from the early-stage products of monoterpenes ($C_{10}H_{16}$) oxidation. Many secondary MTDs, including pinaketone, sabinaketone, limonaketone, norpinone, pinanediol, or 2-hydroxy-3-pinaneone, 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, $\lambda_{max} = 310$ 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 solution. 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 L) contained one of the TAs (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 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 μ l of the reaction solution was saturated with sodium chloride and extracted with 300 μ 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 instrument. For LC-ESI/ToF/MS analyses, each aliquot was filtered through a 0.22 μ m syringe filter (PTFE) and injected into the instrument.

2.4 Chromatographic analyses

2.4.1 Gas chromatography coupled with mass spectrometry

GC/MS analyses were performed with a GC/MS-2010 Ultra gas chromatograph coupled with a single quadrupole mass spectrometer (Shimadzu). Precursors and products of R1—R3 were separated with a VF-WAXms column (Agilent, 30 m $\times$ 0.25 mm $\times$ 0.5 μ m) 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 (30 cm/sec), the purge flow was 2 ml/min, and the linear velocity flow control mode was 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 μ l for all TAs, and the split ratio was set to 20. The MS was operating in scan (m/z = 50-300) and SIM modes. Specific m/z values monitored in SIM mode are provided in Tables S1-S3.

Qualitative analyses were carried out in the NCI mode using methane and ammonia as reagent gases. In these analyses, a ZB-5MSplus column (Zebron, 30 m $\times$ 0.25 mm $\times$ 0.25 μ m) 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 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 analysis time was 32.58 min. The injection volume was 0.5 μ l (splitless mode), and the MS operated in the scan mode (m/z = 50-300).

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

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 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 $\times$ 2.1 mm $\times$ 1.7 μ m. Eluent A was a 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: 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 runtime was 27 min. Elemental compositions
200 were assigned to the detected TACs, assuming they were singly charged, deprotonated pseudo-molecular ions $[M-H]^-$
composed of C, H, and O atoms.

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
205 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
210 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
215 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 $k_{OH_{aq}}$ 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
220 rate coefficient $k_{OH_{aq}}$ ($\text{M}^{-1}\text{s}^{-1}$) for a given molecule is derived as a sum of site-specific values – Fig. 2.

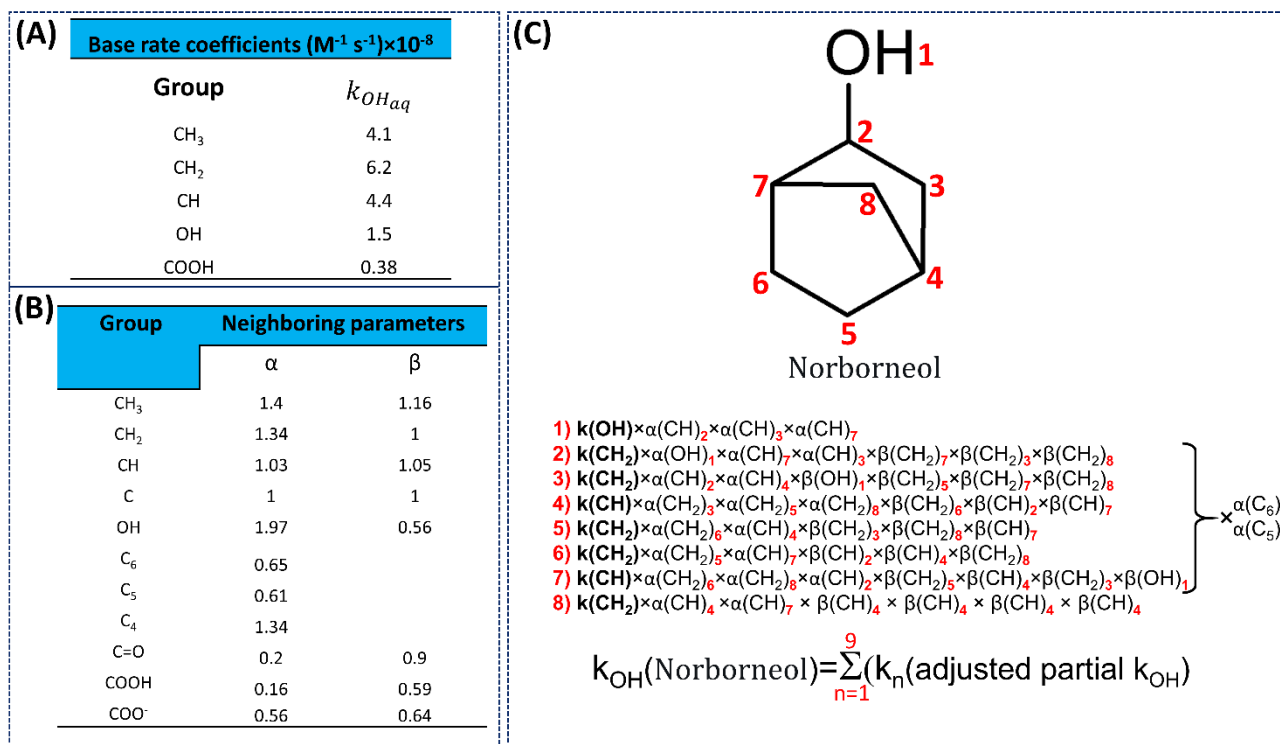


Figure 2: Structure-activity relationship parameters: base rate coefficients (A), neighbouring factors (B), and (C) an example of deriving partial and total $k_{OH_{aq}}$ values for norborneol. (B) values of neighboring factors >1 correspond to activation, whereas values <1 indicate a deactivating effect.

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 CH_x 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 $1\ m^3$ 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 H_2O_2 to the reaction solution confirmed that the TAs under investigation were not photolyzed with the UVB radiation used to generate OH (section 2.2). Also, no interactions were observed between the precursors and H_2O_2 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).

3 Results and discussion

3.1 Analysis of products

270 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.

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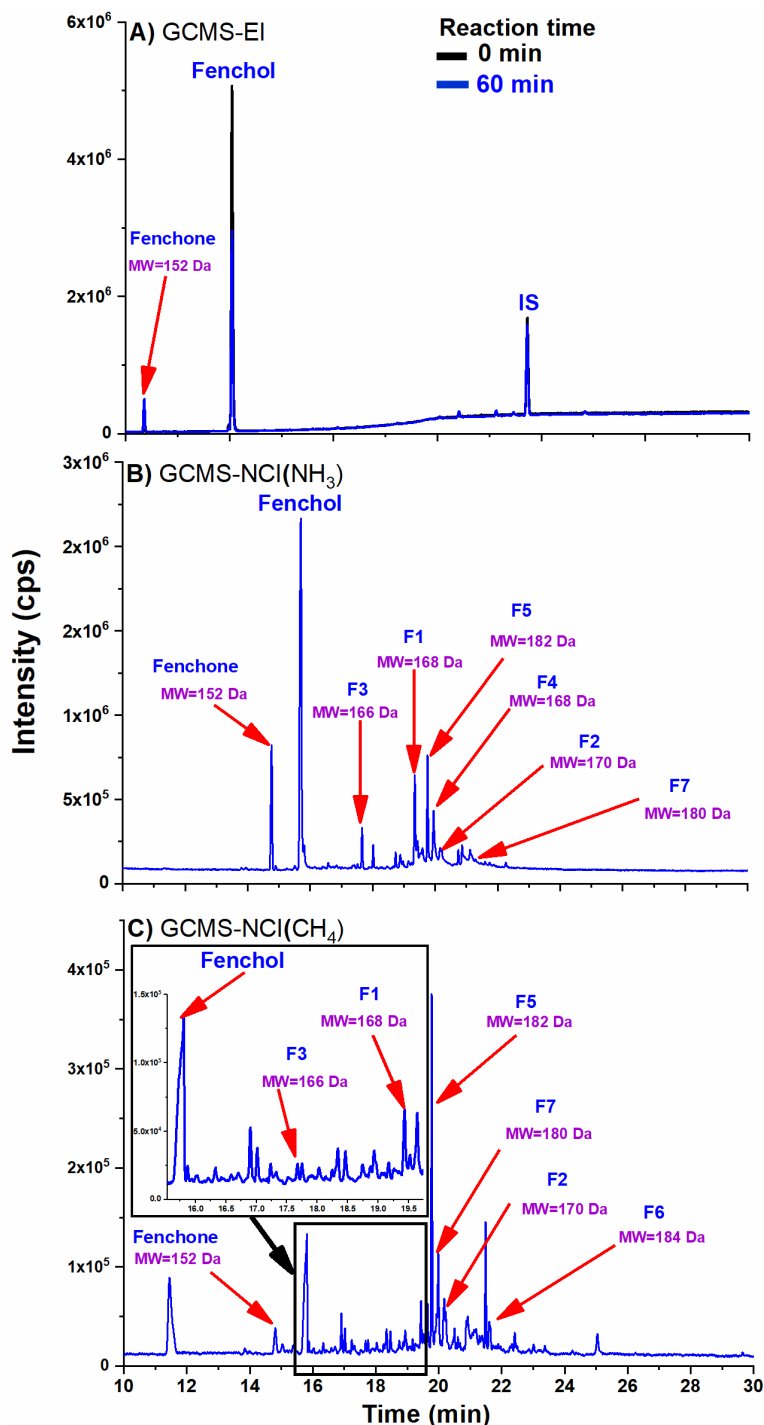


Figure 3: GC/MS chromatograms of the products of fenchol (FCH) + OH reaction (R1) detected with EI (A) and NCI using NH₃ (B), and CH₄ (C) as reagent gases. Note that different chromatographic columns were used for GC-EI/MS and GC-NCI/MS analyses (section 2.4.1), resulting in different retention times between chromatograms acquired using different ionization modes.

In the EI mode, only the formation of fenchone from R1 was observed (Fig. 3A). Many additional products were detected with NCI (Fig. 3B and C), due to the higher overall sensitivity for products F1-F7 in this mode (Javelle and Righezza and Danger, 2021). Very similar results were obtained for both reagent gases, but the sensitivity was about 10-times higher for NH₃. For this reason, non-acidic products of R1—R3 were 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, LC-ToF/MS was used to study the formation of TACs – results for R1 are presented in Fig. 4, and data for R2 and R3 are provided in Figs. S3 and S4.

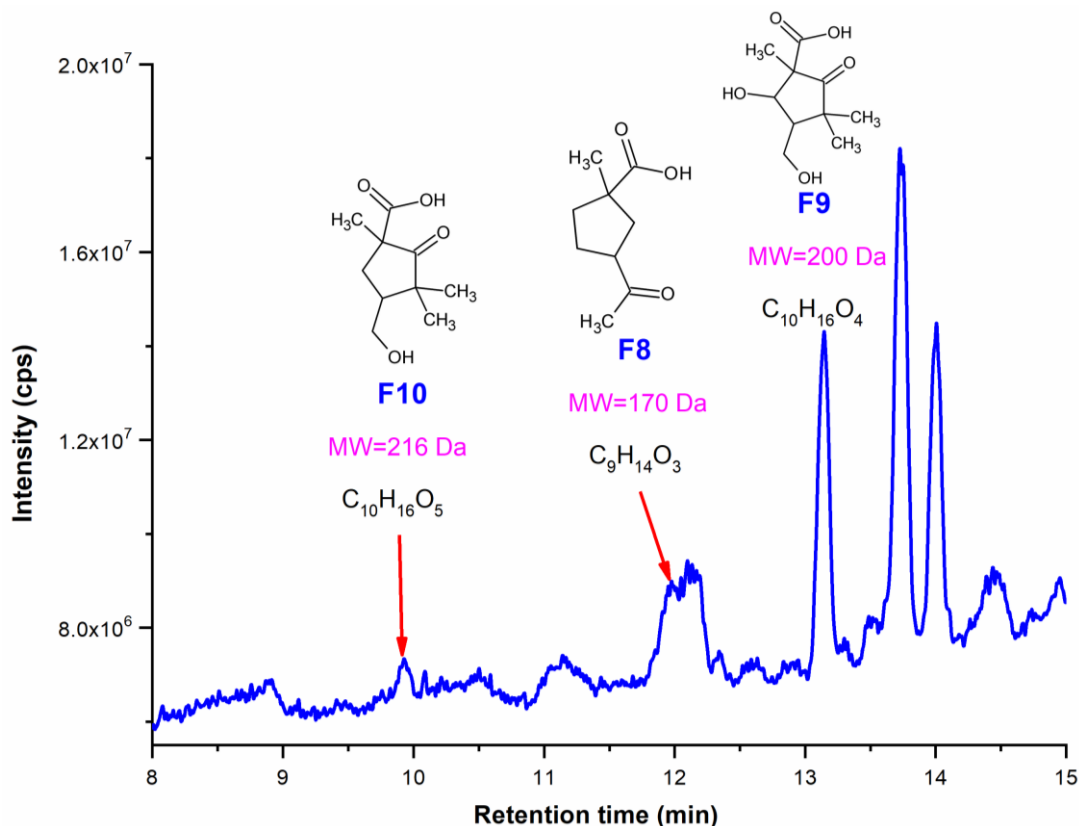


Figure 4: LC-ToF/MS chromatogram of TACs formed from OH reaction with fenchol – R1.

Results of LC-ToF/MS analysis confirmed the formation of TACs from R1—R3. Elemental compositions of detected TACs were assigned based on the acquired high-resolution MS spectra and are provided in Tables S13-S15. In general, the results of chromatographic analyses confirmed that the mechanisms of R1—R3 involved the addition of oxygenated moieties to the carbon backbone of the precursors, similar to the same reactions previously investigated in the gas-phase (Ceacero-Vega et al., 2012).

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.

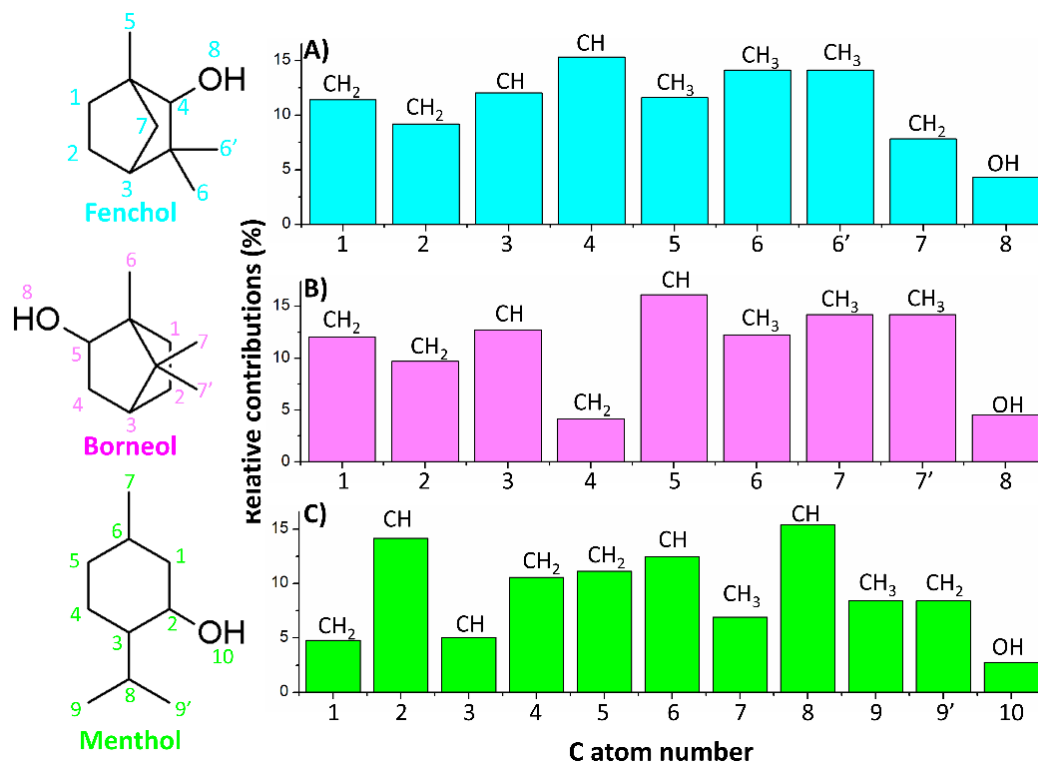


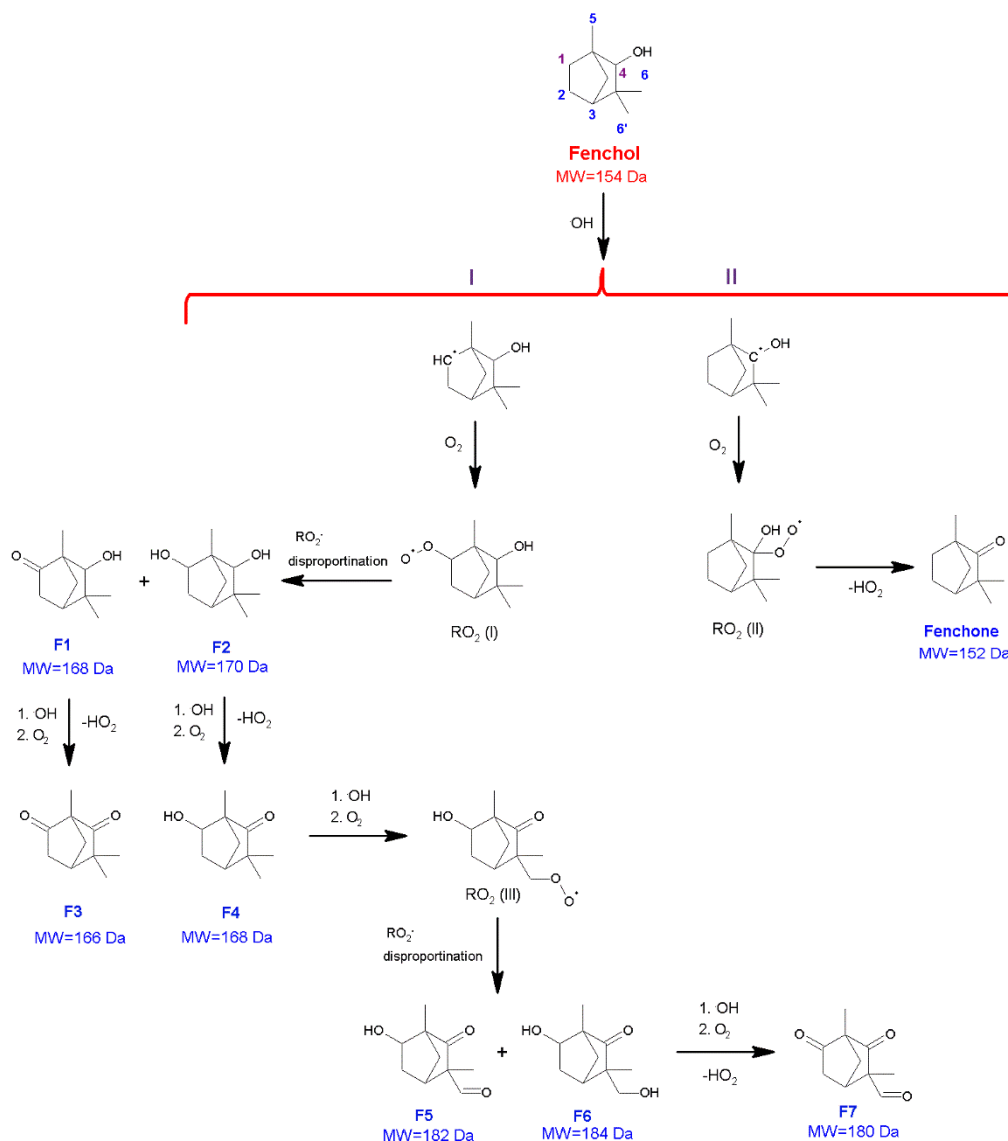
Figure 5: The relative values of partial rate coefficients for the aliphatic H—atom abstraction from fenchol (A), borneol (B), and menthol (C) predicted with SAR (section 2.6). SAR results for all reactants are provided in Tables S4-S6.

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 CH_x 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).

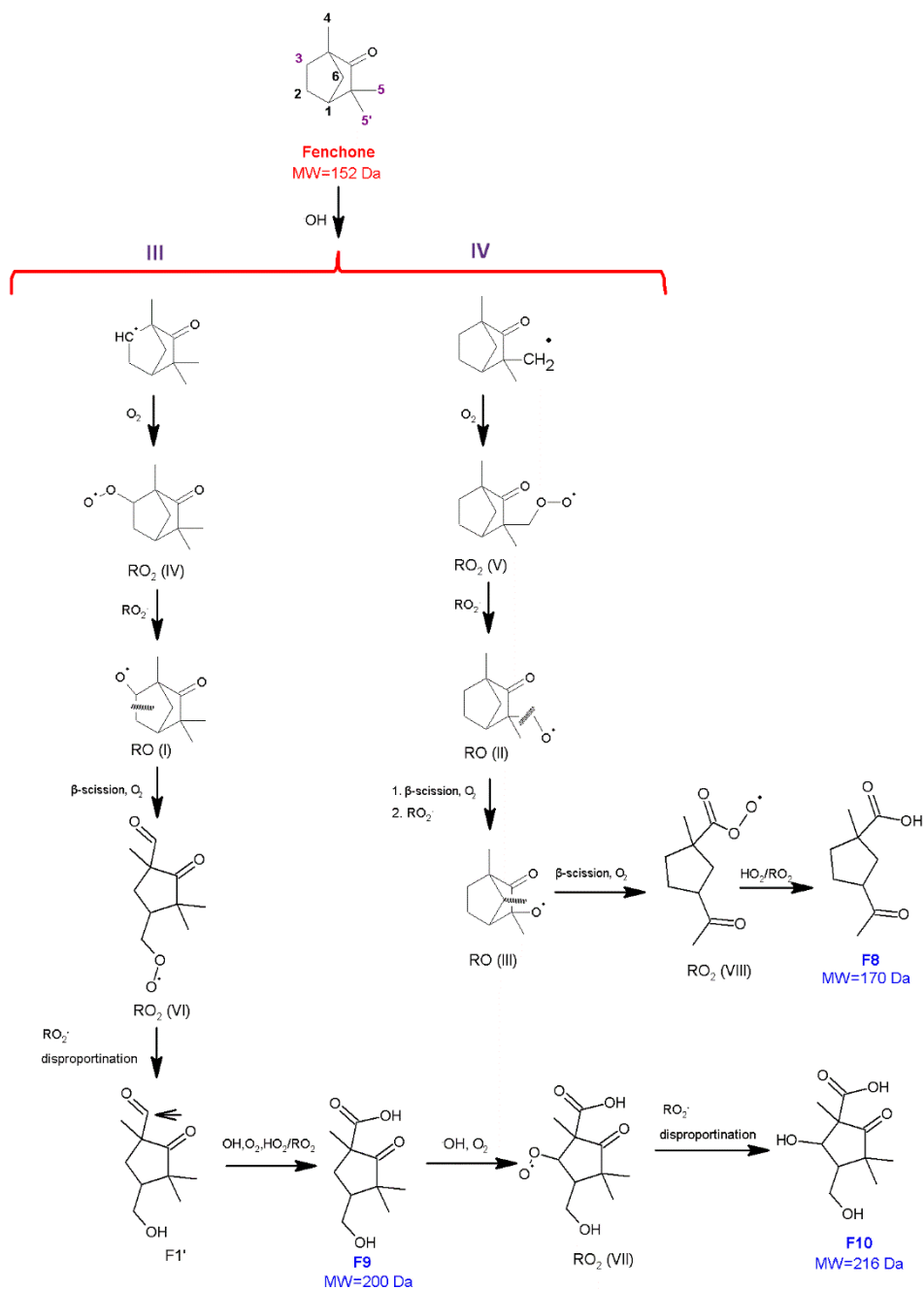


Scheme 1: Proposed mechanism of fenchol + OH reaction (R1). The products tentatively identified in this work are highlighted in blue bold font. All possible pathways and isomeric products were not included for clarity. The mechanism of R1 is continued in Scheme 2.

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 —OH moiety are among the preferred 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 $k_{\text{OH}_{\text{aq}}}$ values (Table S4) and the total $k_{\text{OH}_{\text{aq}}}$ 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

345 react with OH to yield RO₂(III), which then produces another pair of disproportionation products - F5 and F6 (Russell, 1957). 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 CH₂ group (Table S4). In pathway II, FCH is converted to fenchone by elimination of HO₂ following the H—atom abstraction from the α -position of —OH (Bradley et al., 2001; Puchkov and Buneeva and Perkel', 2005).

350 Considering the known reactions of RO and RO₂ radicals, proposing a mechanism for the formation of TACs detected with LC-ToF/MS (Fig. 4) directly from FCH was difficult. Consequently, in Scheme 2, TACs F8-F10 are produced from the OH reaction with fenchone.



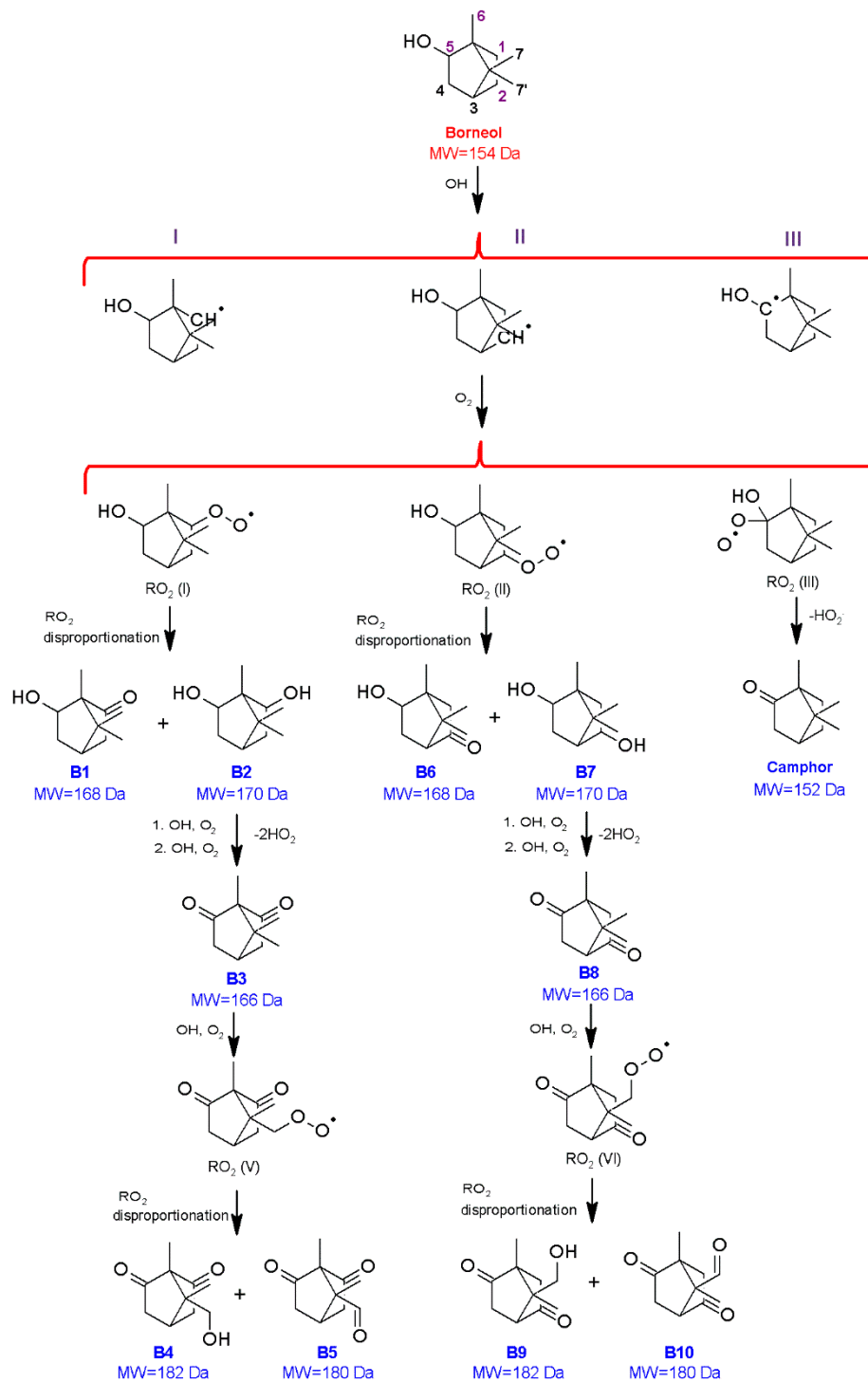
355 **Scheme 2: Proposed mechanism for the OH reaction with fenchone. Terpenoic acids detected with LC-ToF/MS are highlighted in bold blue font.**

Partial $k_{OH_{aq}}$ 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, RO₂(IV), and RO₂(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
RO₂(IV), which then undergoes a β -scission reaction, resulting in RO₂(VI). RO₂(VI) yields by-product 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 RO₂(V), which forms F8, following two consecutive β -scission reactions (Enami and Sakamoto, 2016).

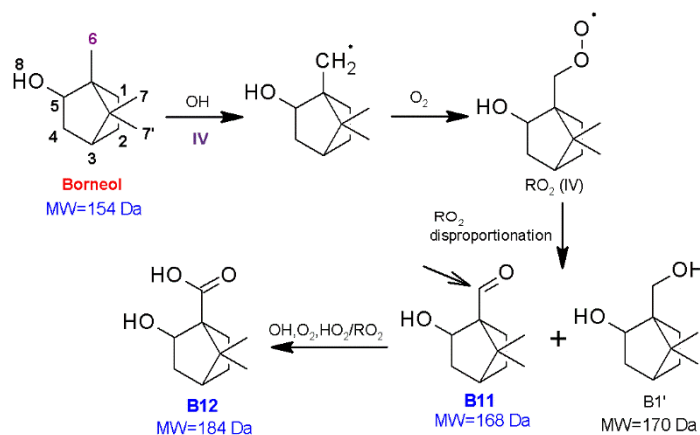
3.2.2 Mechanism of OH reaction with borneol

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.



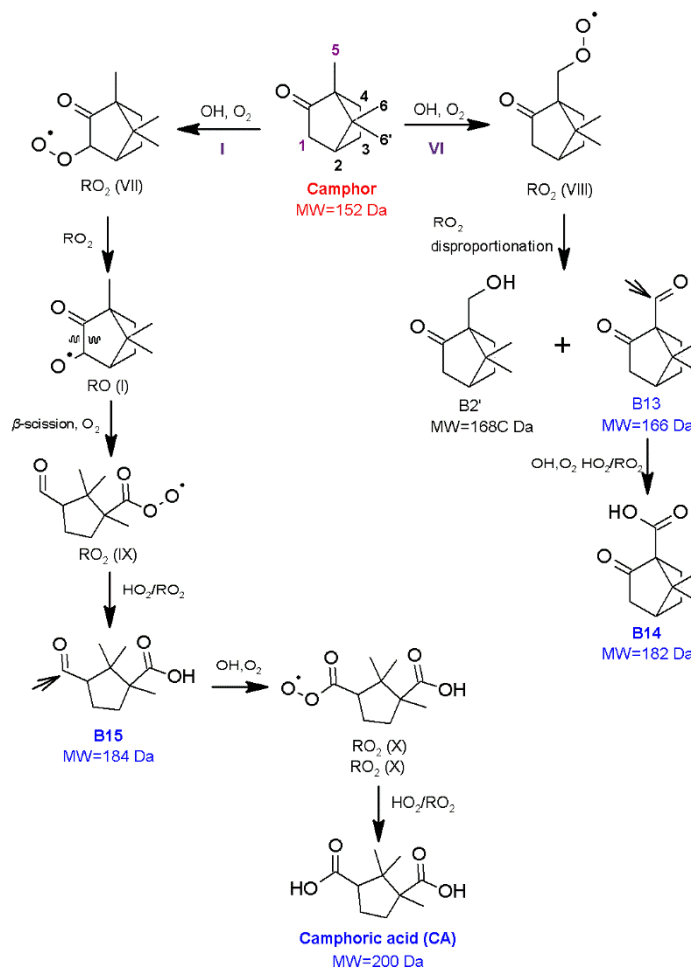
Scheme 3: Proposed mechanism of borneol (BNL) + OH reaction (R2). The detected products are highlighted in bold blue font. The formation of all possible isomers is not included for clarity. The mechanism of R2 is continued in Schemes 4 and 5 – formation of TACs.

In Scheme 3, RO₂(I) and RO₂(II) are formed via pathways I and II, respectively. Formation of B1-B2 and B6-B7 can be explained via disproportionation reactions of RO₂(I) and RO₂(II) (Russell, 1957). According to SAR, diols: B2 ($k_{OH_{aq}} = 3.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), B7 ($k_{OH_{aq}} = 3.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) are oxidized faster than B1 ($k_{OH_{aq}} = 2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and, B6 ($k_{OH_{aq}} = 2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Witkowski et al., 2024). For this reason, in Scheme 3, dicarbonyls B3 and B8 are formed 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 B2 and B7 was among the major reaction channels for these products. The conversion of BNL into camphor (pathway III in Scheme 3) likely occurs via an analogous mechanism (Denisov and Khudyakov, 1987; Puchkov and Buneeva and Perkel', 2005; Puchkov et al., 2013; Bradley et al., 2001). Even though the formation of TACs detected with LC/MS (see Fig. S3) from camphor is mechanistically more likely, the acidic product B12 may also be produced directly from BNL, involving the H—atom abstraction from position 6 – Scheme 4.



Scheme 4: Formation of B12 from OH reaction with borneol (R2) via pathway IV, involving the H—atom abstraction from position 6.

In Scheme 4, pathway (IV) yields RO₂(VI), which undergoes the disproportionation reaction, resulting in B1' and B1' and B11, the latter of which is further oxidized to B12 (Enami and Sakamoto, 2016). The two by-products formed by pathway (IV) – B11 and B1' - were not detected, likely due to their low formation yields and rapid conversion of B11 to B12. Camphoric acid and B14, formed from R2, were most likely produced from camphor – Scheme 5.

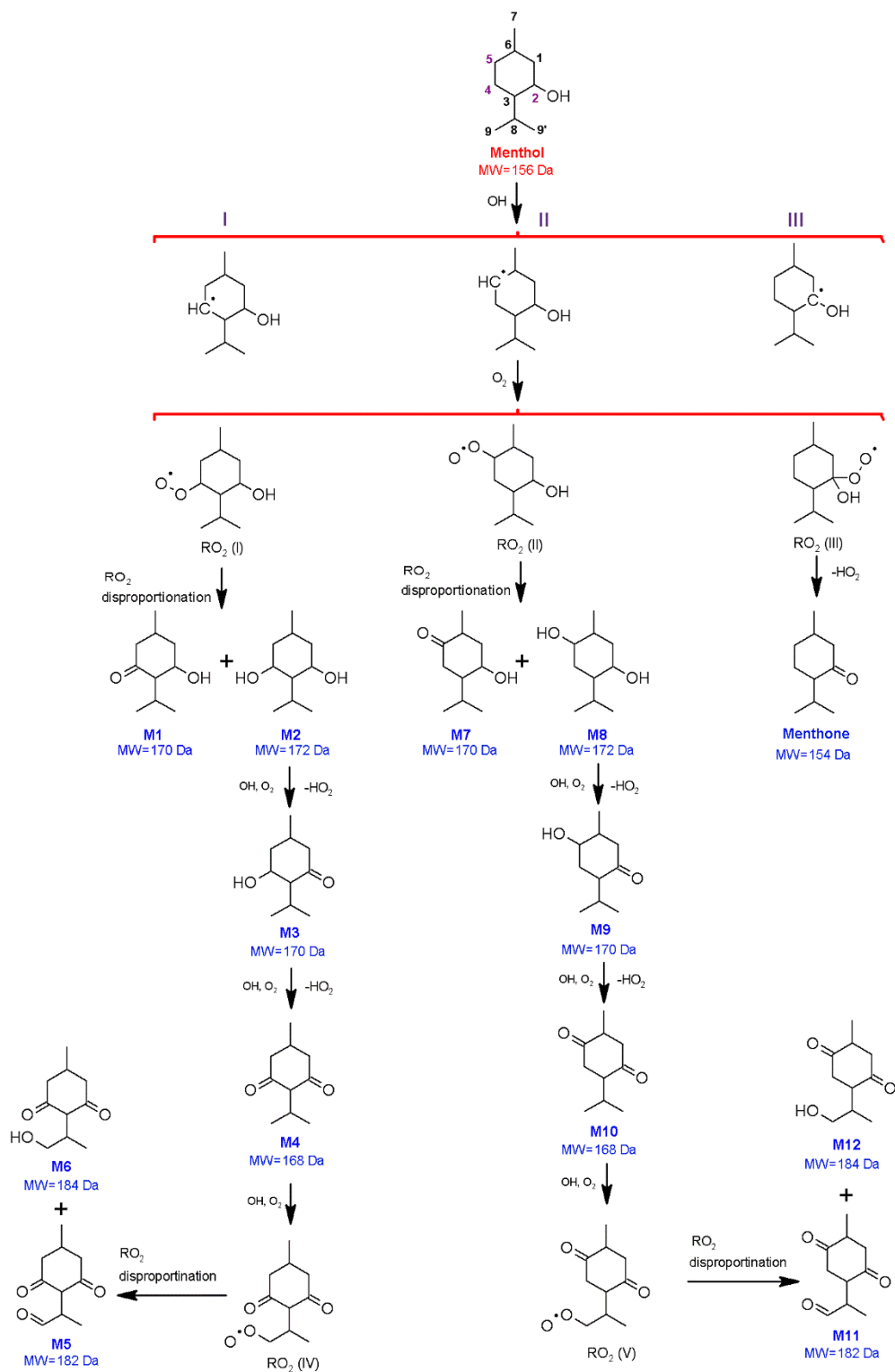


Scheme 5: Proposed mechanism for OH reaction with camphor. The products detected (camphoric acid and B14) are highlighted in bold blue font.

395 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).

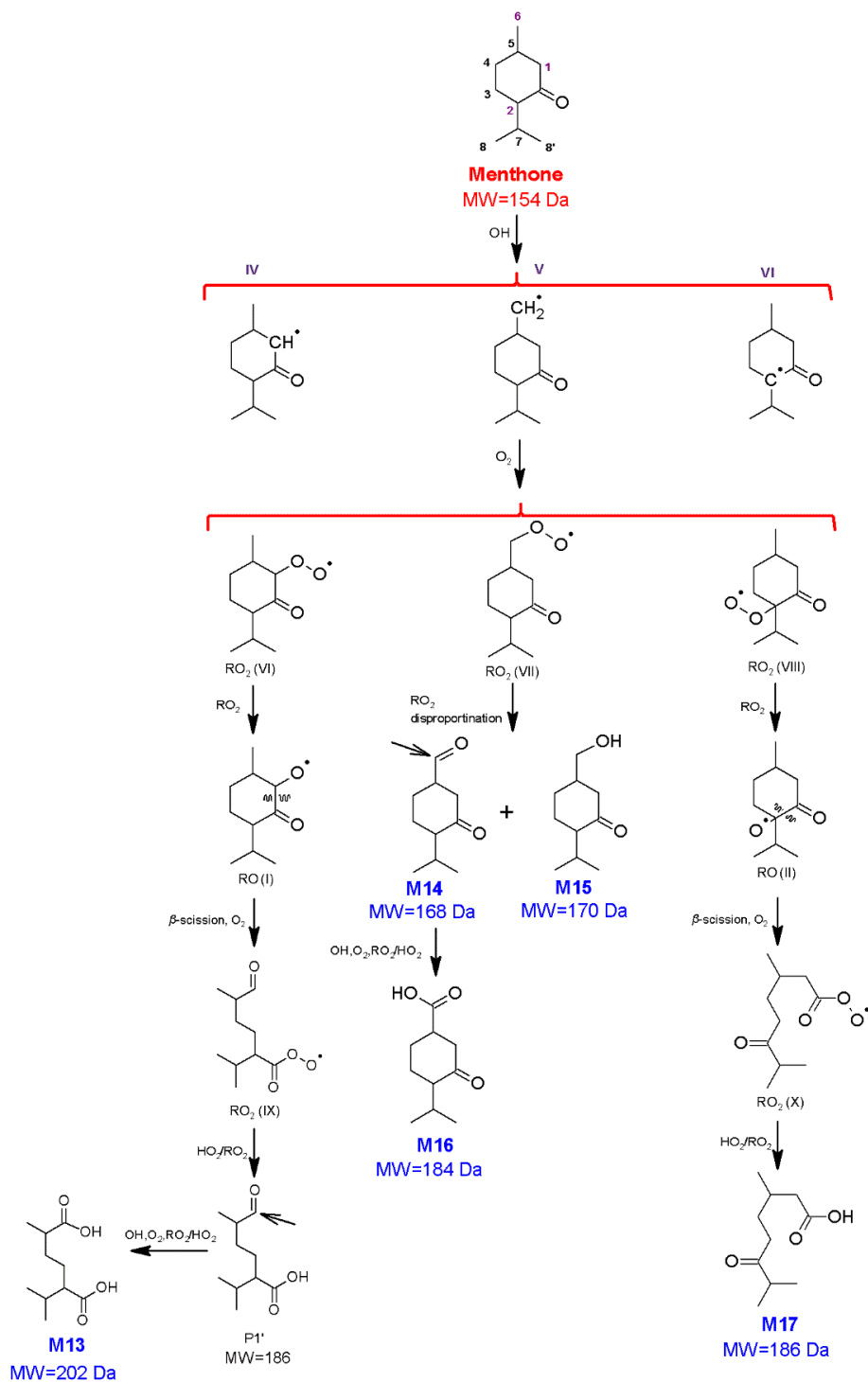
400 3.2.3 Mechanism of OH reaction with menthol

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.



405 **Scheme 6: Proposed mechanism of menthol (MTH) + OH reaction (R3). Products observed in this work are highlighted in bold blue 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: M1, M7, and M2, M8. Afterward, M3 and M9 are formed in Scheme 6 by
410 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 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-
415 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.



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

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 C₆ ring opening via the β -scission reaction and disproportionation of resulting RO₂ 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 in this work. 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 TAs under investigation, the major products were non-acidic molecules containing —OH and C=O moieties, and the yields of TACs ranged from 1 to 5% – Table. 1.

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

Precursor	Product yields		
	Non-acidic ^a	Acids ^b	Total
Fenchol	0.91±0.27	0.03±0.02	0.94±0.39
Borneol	0.95±0.27	0.05±0.02	0.99±0.28
Menthol	0.87±0.26	0.01±0.005	0.88±0.26

^aMeasured with authentic or surrogate standards ^bValues obtained from the kinetic models

The yields of TACs from R1-R3 obtained in this work are comparable with the data obtained for OH reaction with terpenoic 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 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 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
<i>Alcohol (precursor)</i>	<i>Ketone (product)</i>	<i>Aqueous phase</i>	<i>Gas-phase</i>	
Fenchol	Fenchone	0.11±0.01	0.61±0.03	(Ceacero-Vega et al., 2012)
Borneol	Camphor	0.12±0.02	0.49±0.01	(Ceacero-Vega et al., 2012)
Menthol	Menthone	0.03±0.003	-	
Cyclohexanol	Cyclohexanone	-	0.55±0.06	(Bradley et al., 2001)

^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 $k_{OH_{gas}}$ values estimated with SAR (Ceacero-Vega et al., 2012), 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 $k_{OH_{aq}}$. 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 S16 and S17) and their proposed formation pathways (Schemes 1-7). Even though the model was based on a simplified mechanism of R1—R3, a good agreement with the experimental data was obtained. Measured and modelled temporal evolution of reactants in R1 is presented in Fig. 6, while data for R2 and R3 are provided in Figs. S6 and S7, respectively.

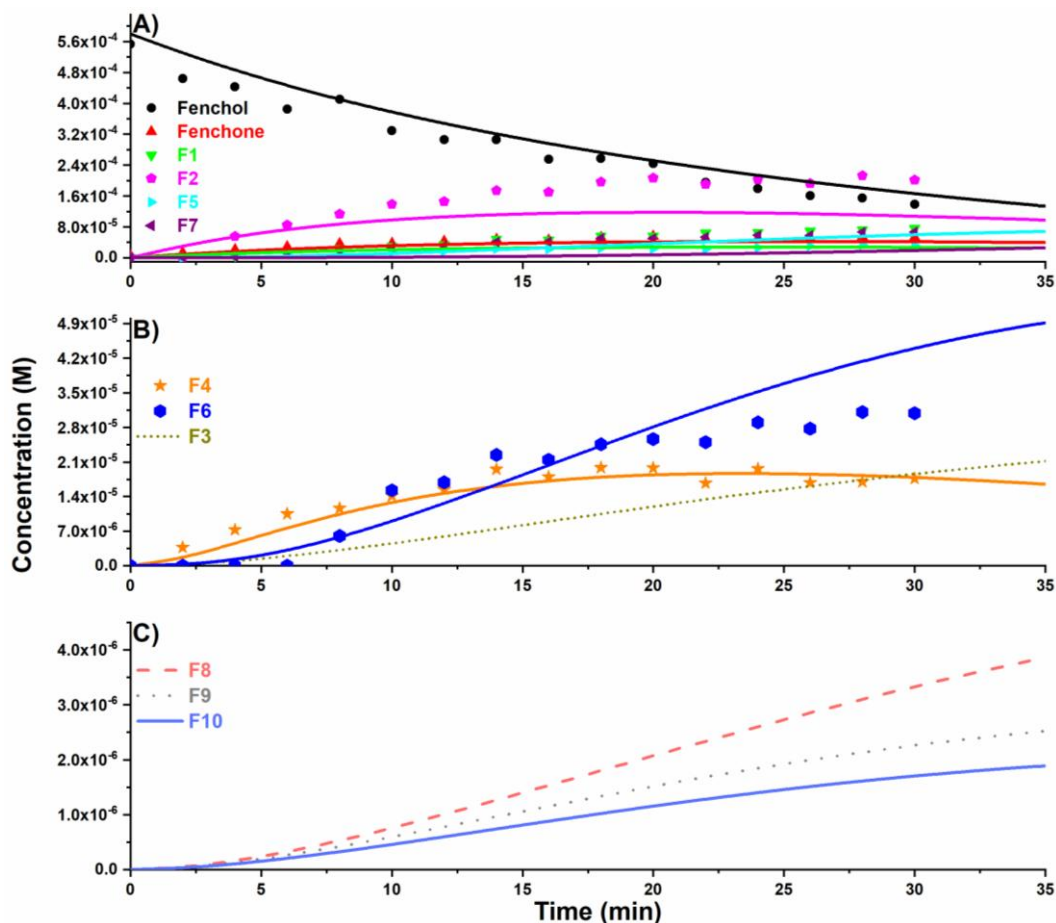


Figure 6: Measured and modeled temporal evolution of the reactants for the fenchol + OH reaction (R1). Points represent experimental data, and lines are the temporal profiles generated by the model. Structures of non-acidic (A and B) and acidic (C) products are shown in Schemes 1 and 2, respectively.

For R1, the box model reproduced the temporal evolution of the reactants with good accuracy (Fig.6A and B) and was used to derive the yields of some products, particularly TACs (Fig. 6C). Only model data are shown for TACs and some non-acidic products since their yields could not be measured (section 2.7). The predicted temporal evolution was combined with H^{cc} values for the reactants to estimate the yields of $_{aq}$ SOAs from R1—R3.

4 Atmospheric implications

As discussed in our previous work, R1—R3 can be relevant in the atmosphere for $LWC \geq 0.1 \text{ g m}^{-3}$ (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 $3.5 \times 10^{-15} \text{ M}$ (urban clouds) and $2.2 \times 10^{-14} \text{ M}$ (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 were obtained for marine clouds with the average $[OH]_{aq} = 2.2 \times 10^{-12}$ 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 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 $[OH]_{aq}$ 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 $_{aq}SOAs$ from R1- R3 were derived with Eq. 2 for LWC values ranging from 0.03 to 3 ($g\ m^{-3}$) - Fig. 7.

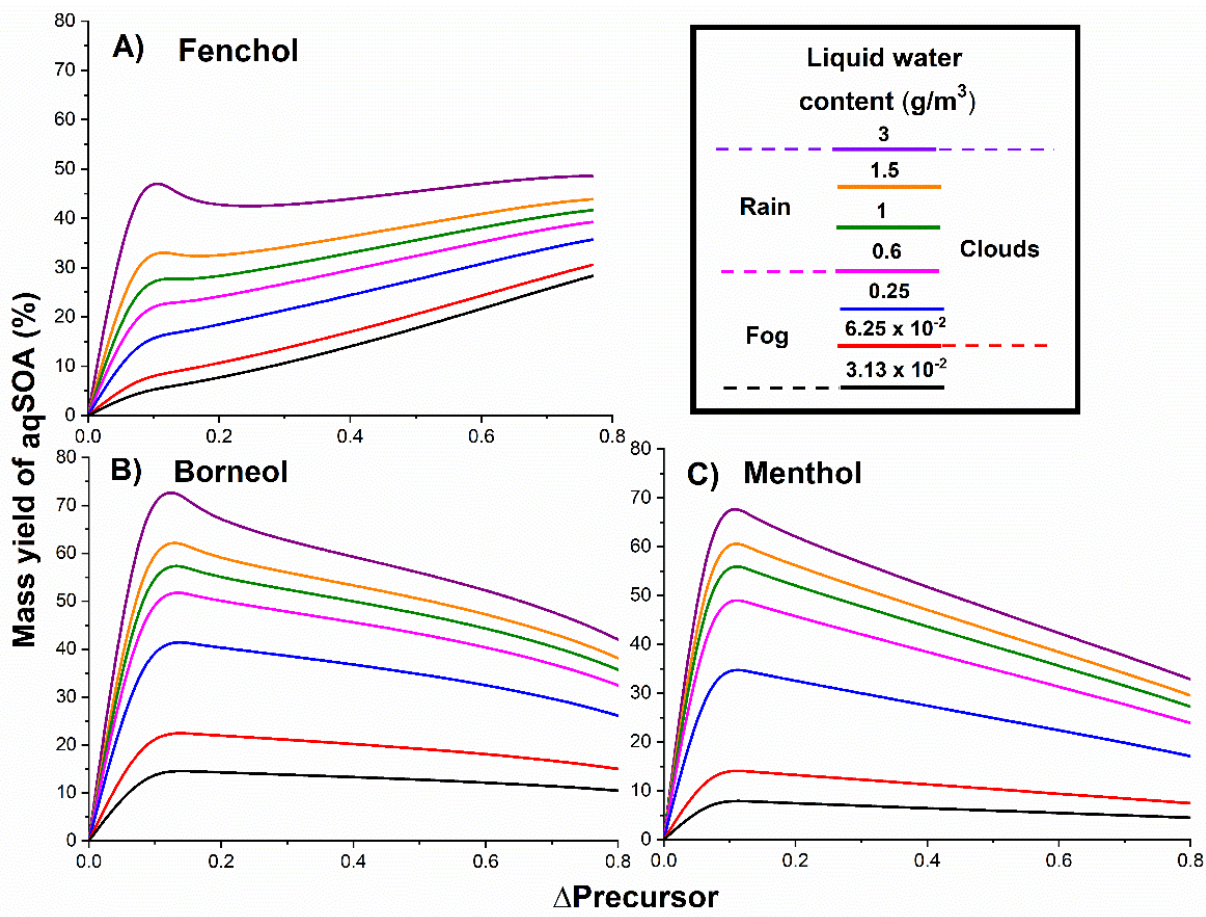


Figure 7: Modelled yields of $_{aq}SOA$ from fenchol (A), borneol (B), and menthol (C) as a function of LWC and reaction coordinate.

495 The main components of aqSOA formed from R1—R3 at LWC between 0.3—3 (g m^{-3}) are the first- and second-generation TACs. However, at higher LWC, the relative contribution of non-acidic products, which were formed with much higher yields than TACs (Table 1), becomes dominant. The initial spikes in the mass yields of aqSOA are also due to the non-acidic products partitioning into the aqueous phase — Fig. 7. An increase in the yield of aqSOA for FCH (Fig. 7A) at the later stages of the reaction was observed, whereas BNL and MTH exhibited the opposite trend (Figs. 7B and C). The trends
500 observed in Fig. 7B 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 (Tables S8 and S9) are completely oxidized and thus removed by the time the precursors are consumed.

The yield of aqSOA from R3 (Fig. 7C) was somewhat lower than that of R2 (Fig. 7B). This can 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
505 yield of aqSOA . 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, oxidation of precursors with bridged C_6 rings yielded less fragmented products (Ceacero-Vega et al., 2012). The increase in aqSOA in Fig. 7A is attributed to the significantly high H^{cc} values of the products of R1, particularly F5, F7, F9, and F10 (see Schemes 1 and 2 and Table S10). Additionally, the formation of highly oxygenated TACs (F9 and F10) from R1 also
510 contributed to the increase in the predicted aqSOA yield in Fig. 7A. Analogous products, with very high H^{cc} values, were not formed from R2 or R3 (Tables S11 and S12).

The modelled yields of aqSOA from R1—R3 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—R3 are comparable with the values obtained for the aqueous
515 OH reaction with terpenoic 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
520 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
525 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 $_{aq}$ SOA flux.

5 Conclusions

This work provides a comprehensive mechanistic and quantitative investigation of aqueous OH reactions with three representative TAs—FCH, BNL, and MTH. The results obtained demonstrate that these semi-volatile oxygenated terpenoids undergo efficient aqueous oxidation, primarily yielding multifunctional, non-acidic products and smaller but atmospherically important fractions of low-volatility terpenoic 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 $_{aq}$ SOA mass yields from terpenoic 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 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 aqSOA . The mechanistic insights and quantitative parameters provide a foundation for 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. 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

The authors declare that they have no conflicts of interest.

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