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1 **The atmospheric impacts of monoterpene ozonolysis on**
2 **global stabilised Criegee intermediate budgets and SO₂**
3 **oxidation: experiment, theory and modelling**

4

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20

21 **Abstract**

22 The gas-phase reaction of alkenes with ozone is known to produce stabilised Criegee
23 intermediates (SCIs). These biradical/zwitterionic species have the potential to act as
24 atmospheric oxidants for trace pollutants such as SO₂, enhancing the formation of sulfate
25 aerosol with impacts on air quality and health, radiative transfer and climate. However, the
26 importance of this chemistry is uncertain as a consequence of limited understanding of the
27 abundance and atmospheric fate of SCIs. In this work we apply experimental, theoretical and
28 numerical modelling methods to quantify the atmospheric impacts, abundance, and fate, of



1 the structurally diverse SCIs derived from the ozonolysis of monoterpenes, the second most
2 abundant group of unsaturated hydrocarbons in the atmosphere. We have investigated the
3 removal of SO₂ by SCI formed from the ozonolysis of three monoterpenes (α -pinene, β -
4 pinene and limonene) in the presence of varying amounts of water vapour in large-scale
5 simulation chamber experiments. The SO₂ removal displays a clear dependence on water
6 vapour concentration, but this dependence is not linear across the range of [H₂O] explored. At
7 low [H₂O] a strong dependence of SO₂ removal on [H₂O] is observed, while at higher [H₂O]
8 this dependence becomes much weaker. This is interpreted as being caused by the production
9 of a variety of structurally (and hence chemically) different SCI in each of the systems
10 studied, each displaying different rates of reaction with water and of unimolecular
11 rearrangement/decomposition. The determined rate constants, $k(\text{SCI}+\text{H}_2\text{O})$, for those SCI that
12 react primarily with H₂O range from $4 - 310 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. For those SCI that predominantly
13 react unimolecularly, determined rates range from $130 - 240 \text{ s}^{-1}$. These values are in line with
14 previous results for the (analogous) stereo-specific SCI system of *syn/anti*-CH₃CHOO. The
15 experimental results are interpreted through theoretical studies of the SCI unimolecular
16 reactions and bimolecular reactions with H₂O, characterised for α -pinene and β -pinene at the
17 M06-2X/aug-cc-pVTZ level of theory. The theoretically derived rates agree with the
18 experimental results within the uncertainties. A global modelling study, applying the
19 experimental results within the GEOS-Chem chemical transport model, suggests that > 98 %
20 of the total monoterpene derived global SCI burden is comprised of SCI whose structure
21 determines that they react slowly with water, and whose atmospheric fate is dominated by
22 unimolecular reactions. Seasonally averaged boundary layer concentrations of monoterpene-
23 derived SCI reach up to $1.2 \times 10^4 \text{ cm}^{-3}$ in regions of elevated monoterpene emissions in the
24 tropics. Reactions of monoterpene derived SCI with SO₂ account for < 1 % globally but may
25 account for up to 50 % of the gas-phase SO₂ removal over areas of tropical forests, with
26 significant localised impacts on the formation of sulfate aerosol, and hence the lifetime and
27 distribution of SO₂.

28

29 1 Introduction

30 Chemical oxidation processes in the atmosphere exert a major influence on atmospheric
31 composition, leading to the removal of primary emitted species, and the formation of
32 secondary products. In many cases either the emitted species or their oxidation products



1 negatively impact air quality and climate (e.g. ozone, which is also a potent greenhouse gas).
2 These reactions can also transform gas-phase species to the condensed phase, forming
3 secondary aerosol that again can be harmful to health and can both directly and indirectly
4 influence radiative transfer and hence climate (e.g. SO₂ oxidation leading to the formation of
5 sulfate aerosol).

6 Tropospheric gas-phase oxidants include the OH radical, ozone, the NO₃ radical, and halogen
7 atoms. Stabilised Criegee intermediates (SCIs), or carbonyl oxides, have been identified
8 as another potentially important oxidant in the troposphere (e.g. Cox and Penkett, 1971;
9 Mauldin et al., 2012). SCIs are thought to be formed in the atmosphere predominantly
10 from the reaction of ozone with unsaturated hydrocarbons, though other processes may
11 be important under certain conditions, e.g. alkyl iodide photolysis (Gravestock et al.,
12 2010), dissociation of the DMSO peroxy radical (Asatryan and Bozzelli, 2008).
13 Laboratory experiments and theoretical calculations have shown SCI to oxidise SO₂ (e.g.
14 Cox and Penkett, 1971; Welz et al., 2012; Taatjes et al., 2013), organic (Welz et al.,
15 2014) and inorganic (Foreman et al., 2016) acids (Vereecken et al., 2017), and a number
16 of other important trace gases found in the atmosphere, as well as forming adducts with
17 NO₂ (Taatjes et al., 2014; Vereecken et al., 2017; Caravan et al., 2017). Measurements in
18 a boreal forest (Mauldin et al., 2012) and at a coastal site (Berresheim et al., 2014) have
19 both identified a ‘missing’ process (in addition to reaction with OH) oxidising SO₂ to
20 H₂SO₄, potentially arising from SCI reactions.

21 Here, we present results from a series of experimental studies into SCI formation and
22 reactions, carried out under atmospheric boundary layer conditions in the European
23 Photochemical Reactor facility (EUPHORE), Valencia, Spain. We examine the ozonolysis of
24 three monoterpenes with very different structures (and hence reactivities with OH and ozone):
25 α -pinene (with an endocyclic double bond), β -pinene (with an exocyclic double bond) and
26 limonene (with both an endo and exo cyclic double bond). We observe the removal of SO₂ in
27 the presence of each alkene-ozone system as a function of water vapour concentration. This
28 allows us to derive relative SCI kinetics for reaction with H₂O, SO₂, and unimolecular
29 decomposition. Further, we calculate absolute unimolecular rates and bimolecular reaction
30 rates with H₂O for all α -pinene and β -pinene derived SCI at the M06-2X/aug-cc-pVTZ level
31 of theory. A global modelling study, using the GEOS-Chem global chemical transport model,



1 is performed to assess global and regional impacts of the chemical kinetics of monoterpene
2 SCI determined in this study.

3 **1.1 Stabilised Criegee Intermediate Kinetics**

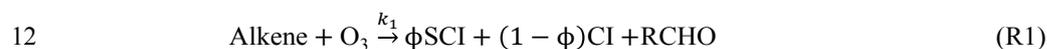
4 Ozonolysis of an unsaturated hydrocarbon produces a primary ozonide that rapidly
5 decomposes to yield pairs of Criegee intermediates (CIs) and carbonyls (Johnson and
6 Marston 2008). The population of CIs are formed with a broad internal energy
7 distribution giving both chemically activated and stabilised forms. Chemically activated
8 CIs may undergo collisional stabilisation to an SCI, unimolecular decomposition or
9 isomerisation. SCIs can have sufficiently long lifetimes to undergo bimolecular reactions
10 (Scheme 1).

11 The predominant atmospheric fate for the simplest SCI, CH_2OO , is reaction with water
12 vapour (likely with the dimer $((\text{H}_2\text{O})_2)$ (e.g. Berndt et al., 2014; Newland et al., 2015a;
13 Chao et al., 2015; Lewis et al., 2015; Lin et al., 2016). For larger SCI, both experimental
14 (Taatjes et al., 2013; Sheps et al., 2014; Newland et al., 2015a; Huang et al., 2015) and
15 theoretical (Kuwata et al., 2010; Anglada et al., 2011; Anglada and Sole, 2016) studies
16 have shown that their kinetics, in particular reaction with water, are highly structure
17 dependent. The significant double bond character exhibited in the zwitterionic
18 configurations of mono-substituted SCI leads to two distinct chemical forms: *syn*-SCI
19 (*i.e.* those where an alkyl-substituent group is on the same side as the terminal oxygen of
20 the carbonyl oxide moiety), and *anti*-SCI (*i.e.* with the terminal oxygen of the carbonyl
21 oxide moiety on the same side as a hydrogen group). The two conformers of CH_3CHOO ,
22 which are both mono-substituted, display these properties. This difference in conformer
23 reactivities has been predicted theoretically (Ryzhkov and Ariya, 2004, Kuwata et al.,
24 2010; Anglada et al., 2011; Lin et al., 2016) and was subsequently confirmed
25 experimentally (Taatjes et al., 2013; Sheps et al., 2014) for the two CH_3CHOO
26 conformers. The significantly faster reaction of *anti*- CH_3CHOO with water is driven by
27 the higher potential energy of this isomer, while more stable SCI, with a methyl group in
28 *syn*-position, such as *syn*- CH_3CHOO or $(\text{CH}_3)_2\text{COO}$, react orders of magnitude more
29 slowly with water.

30 SCI can also undergo unimolecular isomerisation/decomposition in competition with
31 bimolecular reactions. This is likely to be a significant atmospheric sink for *syn*-SCI because



1 of their slow reaction with water vapour (e.g. Huang et al., 2015). Unimolecular reactions of
 2 *syn*-CI/SCI are dominated by a 1,4-H-shift, forming a vinyl hydroperoxide (VHP)
 3 intermediate (Niki et al., 1987; Rickard et al., 1999; Martinez and Herron, 1987; Johnson and
 4 Marston, 2008; Kidwell et al., 2016). Decomposition of the VHP formed in this process is an
 5 important non-photolytic source of OH, HO₂, and RO₂ in the atmosphere (Niki et al.,
 6 1987; Alam et al., 2013; Kidwell et al., 2016), which can also lead to secondary organic
 7 aerosol formation (Ehn et al., 2014). Unimolecular reactions of the *anti*-CI/SCI are
 8 thought to be dominated by a 1,3-ring closure, the “acid/ester channel”, in which the
 9 CI/SCI decomposes, through a rearrangement to a dioxirane intermediate, producing a
 10 range of daughter products and contributing to the observed overall HO_x radical yield
 11 (Kroll et al., 2002; Johnson and Marston, 2008; Alam et al., 2013).



18 Decomposition of the simplest SCI, CH₂OO, is slow (< 10 s⁻¹) and is not likely to be an
 19 important sink in the troposphere (e.g. Newland et al., 2015a; Chhantyal-Pun et al., 2015).
 20 This decomposition occurs primarily via rearrangement through a ‘hot’ acid species, which
 21 represents the lowest accessible decomposition channel (Gutbrod et al., 1996; Alam et al.,
 22 2011; Chen et al., 2016). However, recently determined unimolecular reaction rates of larger
 23 *syn*-SCI are considerably faster. Newland et al. (2015a) reported unimolecular reaction rate
 24 constants for *syn*-CH₃CHOO of 348 (± 332) s⁻¹ and for (CH₃)₂COO of 819 (± 190) s⁻¹
 25 (assuming $k(\text{syn-CH}_3\text{CHOO}+\text{SO}_2) = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Sheps et al., 2014) and
 26 $k((\text{CH}_3)_2\text{COO}+\text{SO}_2) = 1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Huang et al., 2015), respectively). Smith et al.
 27 (2016) measured the unimolecular decomposition rate of (CH₃)₂COO to be 269 (± 82) s⁻¹ at
 28 283 K increasing to 916 (± 56) s⁻¹ at 323 K, suggesting the rate to be fast and highly
 29 temperature dependent. Novelli et al. (2014), estimated a significantly slower decomposition



1 rate for *syn*-CH₃CHOO of 20 (3-30) s⁻¹ from direct observations of OH formation, while
2 Fenske et al. (2000), estimated the decomposition rate of CH₃CHOO (i.e. a mix of *syn* and
3 *anti* conformers) produced from ozonolysis of *trans*-but-2-ene to be 76 s⁻¹ (accurate to within
4 a factor of three).

5

6 1.2 Monoterpene Ozonolysis

7 Monoterpenes are volatile organic compounds (VOCs) with the general formula C₁₀H₁₆,
8 which are emitted by a wide range of vegetation, particularly from boreal forests. Total global
9 monoterpene emissions are estimated to be 95 (± 3) Tg yr⁻¹ (Sindelarova et al., 2014) -
10 roughly 13 % of total non-methane biogenic VOC emissions. Monoterpene emissions are
11 dominated by α-pinene, which accounts for roughly 34 % of the total global emissions, while
12 β-pinene and limonene account for 17 % and 9 % respectively (Sindelarova et al., 2014).
13 Monoterpenes (mainly α-pinene and limonene) are also present in indoor environments, in
14 significant amounts where cleaning products and air fresheners are in routine use (on the
15 order of 100s of ppbv) (e.g. Singer et al., (2006); Sarwar and Corsi, (2007)), where their
16 ozonolysis products can affect indoor chemistry and health (e.g. Rossignol et al., (2013);
17 Shallcross et al., (2014)).

18 Monoterpenes are highly reactive due to the presence of (often multiple) double bonds. The
19 oxidation of monoterpenes yields a wide range of multi-functional gas-phase and aerosol
20 products. This process can be initiated by OH and NO₃ radicals or by O₃, with ozonolysis
21 having been shown to be particularly efficient at generating low volatility products that can
22 form SOA, even in the absence of sulfuric acid (e.g. Ehn et al., 2014; Kirkby et al., 2016).
23 These highly oxygenated secondary products have received considerable attention in recent
24 years because of their role in affecting the climate through absorption and scattering of solar
25 radiation (the direct aerosol effect). They can also increase cloud condensation nuclei
26 concentrations, which can change cloud properties and lifetimes (the indirect aerosol effect).
27 They have also been shown to have a wide range of deleterious effects on human health (e.g.
28 Pöschl and Shiraiwa, 2015).

29 The ozonolysis reaction for monoterpenes is expected to follow a similar initial process to
30 that of smaller alkenes, with cyclo-addition at a double bond giving a primary ozonide (POZ),
31 followed by rapid decomposition of the POZ to yield a CI and a carbonyl (Scheme 1).



1 Stabilisation of the large POZs formed in monoterpene ozonolysis is expected to be
2 negligible (Nguyen et al., 2009). However, a major difference in ozonolysis at endocyclic
3 bonds is that, on decomposition of the POZ, the carbonyl oxide and carbonyl moieties are
4 tethered as part of the same molecule, providing the potential for further interaction of the
5 two. These can react together to form secondary ozonides (SOZ), which may be stable for
6 several hours (Beck et al., 2011). However, while this has been shown to be potentially the
7 major fate in the atmosphere for SCI derived from sesquiterpenes (C₁₅H₂₄) (e.g. Nguyen et al.,
8 2009b; Beck et al., 2011; Yao et al., 2014), formation of SOZ is predicted to be small for
9 monoterpene derived SCI because of the high ring strain caused by the tight cyclisation (e.g.
10 Nguyen et al., 2009b). Chuong et al. (2004) predicted formation of a SOZ to become the
11 dominant atmospheric fate for SCI formed in the ozonolysis of endo-cyclic alkenes with a
12 carbon number between 8 and 15, while Vereecken and Francisco (2012) suggested that
13 internal SOZ formation is likely to be limited to product rings containing six or more carbons
14 due to ring strain.

15 No studies have yet directly determined the reaction rates of the large SCI produced from
16 monoterpene ozonolysis with SO₂ (or any other trace gases). This is owing to the
17 complexities of synthesizing and measuring large SCI. However, Ahrens et al. (2014)
18 concluded that the reaction of the C₉-SCI formed in β-pinene ozonolysis with SO₂ is as fast
19 as that determined by Welz et al. (2012) and Taatjes et al. (2013) for CH₂OO and CH₃CHOO
20 respectively (ca. $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) by fitting to the decay of SO₂ in the presence of the
21 ozonolysis reaction. Mauldin et al. (2012) calculated significantly slower reaction rates for an
22 additional oxidant (assumed to be SCI) derived from α-pinene and limonene ozonolysis, with
23 $k(\text{SCI}+\text{SO}_2)$ determined to be $6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for α-pinene and limonene
24 derived SCI respectively. However, it seems likely that the rates calculated by Mauldin et al.
25 (2012) may be substantially underestimated due to the assumption of a very long SCI lifetime
26 (0.2 s) in experiments that were performed at 50 % RH. The calculated rates scale linearly
27 with SCI lifetime and based on reaction rates of smaller SCI with H₂O (reported since the
28 Mauldin et al. work, e.g. Taatjes et al., 2013) it seems likely that the lifetime of the SCI in
29 their experiments would have been more like $0.1 - 2 \times 10^{-2} \text{ s}$, increasing the calculated rate
30 constants by more than an order of magnitude, bringing them into much closer agreement
31 with the rates reported by Ahrens et al. (2014).

32 Unimolecular reactions of the monoterpene SCI are expected to proceed rapidly through the
33 VHP route if a hydrogen is available for a 1,4 H-shift. Those SCI that cannot undergo this



1 rearrangement may undergo unimolecular reactions via the formation of the dioxirane
2 intermediate, but this is expected to be a much slower process (Nguyen et al., 2009). In
3 contrast to smaller SCI, it has been observed experimentally, and predicted theoretically, that
4 the VHP route will mainly lead to rearrangement to an acid (also yielding an OH radical)
5 rather than decomposition of the molecule (e.g. Ma et al., 2008, Ma and Marston, 2008). As
6 for the smaller alkenes, monoterpene ozonolysis has been shown to be a source of HO_x (e.g.
7 Paulson et al., 1997; Alam et al., 2013), predominantly via the VHP rearrangement. The
8 MCMv3.3.1 (Jenkin et al., 2015) applies OH yields of 0.80, 0.35 and 0.87 for α -pinene, β -
9 pinene and limonene respectively.

10 1.2.1 α -pinene derived SCI

11 Decomposition of the α -pinene POZ yields four different C₁₀ Criegee intermediates (Scheme
12 2: CI-1a, 1b, 2a, 2b), with the carbonyl oxide moiety at one end and a carbonyl group at the
13 other. Here, CI-1 is a mono-substituted CI for which both *syn* (1a) and *anti* (1b) conformers
14 exist, while the other, CI-2, is di-substituted, for which two *syn*-conformers (2a and 2b) exist.
15 Ma et al. (2008) infer a relative yield of 50 % for the two basic CI formed, based on the
16 observation that norpinonic acid yields from the ozonolysis of α -pinene and an enone, which
17 upon ozonolysis yields CI-1, are almost indistinguishable.

18 The total SCI yield from α -pinene was determined to be 0.15 (\pm 0.07) by Sipilä et al. (2014)
19 in indirect experiments measuring the production of H₂SO₄ from SO₂ oxidation in the α -
20 pinene ozonolysis system. Drozd and Donahue (2011) also determined a total SCI yield of
21 about 0.15 at 740 Torr, from measuring the loss of hydrofluoroacetone in ozonolysis
22 experiments in a high pressure flow system. The MCMv3.3.1 (Jenkin et al., 1997; Saunders et
23 al., 2003; Jenkin et al., 2015) applies a value of 0.20 based on stabilisation of only the mono-
24 substituted CI-1.

25 1.2.2 β -pinene derived SCI

26 β -pinene ozonolysis yields two distinct conformers of the nopinone C₉-CI (Scheme 3: CI-3
27 and CI-4), which differ in orientation of the carbonyl oxide group, and CH₂OO. CI-3 and CI-4
28 are formed in roughly equal proportions with very little inter-conversion between the two
29 (Nguyen et al., 2009). The difference in the chemical behaviour of CI-3 and CI-4, which were
30 often not distinguished in earlier studies, arises from the inability of the carbon attached to the
31 four-membered ring to undergo the 1,4-H-shift that allows unimolecular decomposition via



1 the VHP channel. This was noted in Rickard et al. (1999) as being a reason for the
2 considerably lower OH yield (obtained via the VHP route) from β -pinene ozonolysis
3 compared to that of α -pinene. This difference leads to contrasting unimolecular
4 decomposition rates for the two CI, with Nguyen et al. (2009) predicting a loss rate of *ca.* 50
5 s^{-1} for CI-3 (via a VHP) and *ca.* 1 s^{-1} for CI-4 (via ring closure to a dioxirane). This result is
6 qualitatively consistent with the experimental work of Ahrens et al. (2014), who determine a
7 ratio of 85:15 for the abundance of SCI-4:SCI-3 about 10 s after the initiation of the
8 ozonolysis reaction, as a consequence of the much faster decomposition rate of SCI-3. Thus
9 the potential for bimolecular reactions to compete with decomposition of SCI-3 and SCI-4 in
10 the atmosphere is very different.

11 Nguyen et al. (2009) theoretically calculate a total SCI yield from β -pinene ozonolysis of 42
12 %, consisting of 16.2 % SCI-3, 20.6 % SCI-4, and 5.1 % CH_2OO . Ahrens et al. (2014)
13 assume an equal yield of CI-3 and CI-4 (45 %) with a 10 % yield of CH_2OO ; 40 % of the total
14 C9-CI are calculated to be stabilised at 1 atm. If all of the CH_2OO is assumed to be formed
15 stabilised (e.g. Nguyen et al., 2009) then this gives a total SCI yield of 46 %. Earlier
16 experimental studies have tended to determine lower total SCI yields with Hasson et al.
17 (2001) reporting a total SCI yield of 0.27 from measured product yields (almost entirely
18 nopinone) and Hatakeyama et al. (1984) reporting a total SCI yield of 0.25. Winterhalter et al.
19 (2000) determined a yield of 0.16 (± 0.04) for excited CH_2OO from β -pinene ozonolysis,
20 obtained via the nopinone yield and 0.35 for the stabilised C9-CI, giving a total SCI yield of
21 0.51 if all the CH_2OO is assumed to be stabilised. Also, experimental studies have tended to
22 report higher CH_2OO yields (determined from measured nopinone yields) than theoretical
23 studies. Nguyen et al. (2009) note that this could be because nopinone can also be formed in
24 bimolecular reactions of SCI-4, hence experimental studies may overestimate CH_2OO
25 production. The MCMv3.3.1 incorporates a total SCI yield of 0.25 from β -pinene ozonolysis,
26 with a yield of stabilised C9-CI of 0.102 and a CH_2OO yield of 0.148.

27 1.2.3 Limonene derived SCI

28 Limonene has two double bonds at which ozone can react. Theory suggests that reaction at
29 the endocyclic bond is more likely; Baptista et al. (2011) calculate reaction at the endo-cyclic
30 bond to be 84 – 94 % (dependent on the level of theory applied). Zhang et al. (2006) suggest
31 the reaction at the endo-cyclic double bond to be roughly 25 times faster than at the exo-
32 cyclic bond, i.e. leading to a branching ratio of *ca.* 96 % reaction at the endo bond and the



1 current IUPAC recommendation (IUPAC, 2013) suggests about 95 % of the primary ozone
2 reaction to be at the endo bond. Leungsakul et al. (2005) reported a best fit to measurements
3 from chamber experiments by assuming an 85 % reaction at the endo-cyclic bond and 15 % at
4 the exo-cyclic bond.

5 Ozone reaction at the endo-cyclic bond of limonene produces four different C₁₀ CI (Scheme
6 4: CI-5a, 5b, 6a, 6b). Similar to CI-1 and CI-2 from α -pinene, CI-5 is a mono-substituted CI
7 for which both *syn* (5a) and *anti* (5b) conformers exist, while the other, CI-6, is di-substituted,
8 for which two *syn*-conformers (6a and 6b) exist. Leungsakul et al. (2005) determined a total
9 SCI yield from limonene ozonolysis of 0.34, consisting of CH₂OO (0.05), CI-7 (0.04), CI-5
10 (0.15) and CI-6 (0.11). Sipilä et al. (2014) determined a total SCI yield of 0.27 (\pm 0.12) from
11 indirect experiments measuring the production of H₂SO₄ from SO₂ oxidation in the presence
12 of the limonene-ozone system. The MCMv3.3.1 describes only reaction with ozone at the
13 endocyclic double bond and recommends a total SCI yield of 0.135 with stabilisation of only
14 the mono-substituted CI-5.

15

16 **2 Experimental**

17 **2.1 Experimental Approach**

18 The EUPHORE facility is a 200 m³ simulation chamber used primarily for studying reaction
19 mechanisms under atmospheric boundary layer conditions. Further details of the chamber
20 setup and instrumentation are available elsewhere (Becker, 1996; Alam et al., 2011), and a
21 detailed account of the experimental procedure, summarised below, is given in Newland et al
22 (2015a).

23 Experiments comprised time-resolved measurement of the removal of SO₂ in the presence of
24 the monoterpene-ozone system, as a function of humidity. SO₂ and O₃ abundance were
25 measured using conventional fluorescence and UV absorption monitors, respectively; alkene
26 abundance was determined via FTIR spectroscopy. Experiments were performed in the dark
27 (*i.e.* with the chamber housing closed; $j(\text{NO}_2) \leq 10^{-6} \text{ s}^{-1}$), at atmospheric pressure (*ca.* 1000
28 mbar) and temperatures between 287 and 302 K. The chamber is fitted with large horizontal
29 and vertical fans to ensure rapid mixing (*ca.* 2 minutes). Chamber dilution was monitored via
30 the first order decay of an aliquot of SF₆, added prior to each experiment. Cyclohexane (*ca.*
31 75 ppmv) was added at the beginning of each experiment to act as an OH scavenger, such that



1 SO₂ reaction with OH was calculated to be ≤ 1 % of the total chemical SO₂ removal in all
2 experiments.

3 Experimental procedure, starting with the chamber filled with clean scrubbed air, comprised
4 addition of SF₆ and cyclohexane, followed by water vapour, O₃ (*ca.* 500 ppbv) and SO₂ (*ca.*
5 50 ppbv). A gap of five minutes was left prior to addition of the monoterpene, to allow
6 complete mixing. The reaction was then initiated by addition of the monoterpene (*ca.* 400
7 ppbv for α -pinene and β -pinene, *ca.* 200 ppbv for limonene), and reagent concentrations
8 followed for roughly 30 - 60 minutes; *ca.* 30 – 90 % of the monoterpene was consumed after
9 this time, dependent on the reaction rate with ozone. Four α -pinene + O₃, five β -pinene + O₃,
10 and five limonene + O₃ experiments, as a function of [H₂O], were performed in total. Each
11 individual run was performed at a constant humidity, with humidity varied to cover the range
12 of [H₂O] = 0.1 – 19 × 10¹⁶ molecules cm⁻³, corresponding to an RH range of 0.1 – 28 % (at
13 298 K). Measured increases in [SO₂] agreed with measured volumetric additions across the
14 SO₂ and humidity ranges used in the experiments (Newland et al., 2015a).

15 2.2 Analysis

16 A range of different SCI are produced from the ozonolysis of each of the three monoterpenes
17 (see Schemes 2 – 4), each with their own distinct chemical behaviour (*i.e.* yields, reaction
18 rates); it is therefore not feasible (from these experiments) to obtain data for each SCI
19 independently; consequently, for analytical purposes we necessarily treat the SCI population
20 in a simplified (lumped) manner – see Section 2.2.2.

21 SCI are assumed to be formed in the ozonolysis reaction with a yield ϕ (Reaction R1). They
22 can then react with SO₂, with H₂O, with acids formed in the ozonolysis reaction, with other
23 species present, or undergo unimolecular decomposition, under the experimental conditions
24 applied (Reactions R2 – R5). A fraction of the SCI produced reacts with SO₂. This fraction (f)
25 is the loss rate of the SCI to SO₂ ($k_2[\text{SO}_2]$) compared to the sum of the total loss processes for
26 the SCI (Equation E1) :

$$27 \quad f = \frac{k_2[\text{SO}_2]}{k_2[\text{SO}_2] + k_3[\text{H}_2\text{O}] + k_d + k_5[\text{acid}] + L} \quad (\text{E1})$$

28 Here, L accounts for the sum of any other chemical loss processes for SCI in the chamber,
29 with the exception of reaction with acids these loss processes are expected to be negligible, as



1 discussed later. After correction for dilution, and neglecting other (non-alkene) chemical sinks
2 for O₃, such as reaction with HO₂ (also produced directly during alkene ozonolysis (Alam et
3 al., 2013; Malkin et al., 2010)), which was indicated through model calculations to account
4 for < 0.5 % of ozone loss under all the experimental conditions, the following equation is
5 derived:

$$6 \quad \frac{d\text{SO}_2}{d\text{O}_3} = \phi \cdot f \quad (\text{E2})$$

7 From Equation E2, regression of the loss of ozone ($d\text{O}_3$) against the loss of SO₂ ($d\text{SO}_2$) for an
8 experiment at a given RH determines the product $f \cdot \phi$ at a given point in time. This quantity
9 will vary through the experiment as SO₂ is consumed, and other potential SCI co-reactants are
10 produced, as predicted by Equation E1. A smoothed fit was applied to the experimental data
11 for the cumulative consumption of SO₂ and O₃, ΔSO_2 and ΔO_3 , (as shown in Figure 2) to
12 determine $d\text{SO}_2/d\text{O}_3$ (and hence $f \cdot \phi$) at the start of each experiment, for use in Equation E2.
13 The start of each experiment (*i.e.* when $[\text{SO}_2] \sim 50$ ppbv) was used as this corresponds to the
14 greatest rate of production of the SCI, and hence largest experimental signals (*i.e.* greatest O₃
15 and SO₂ rate of change; greatest precision) and is the point at which the SCI + SO₂ reaction
16 has the greatest magnitude compared with any other potential loss processes for either
17 reactant species (see discussion below).

18 Other potential fates for SCIs include reaction with ozone (Kjaergaard et al., 2013; Vereecken
19 et al., 2014; Wei et al., 2014; Vereecken et al., 2015), with other SCI (Su et al., 2014;
20 Vereecken et al., 2014), carbonyl products (Taatjes et al., 2012), acids (Welz et al., 2014), or
21 with the parent alkene (Vereecken et al., 2014; Decker et al., 2017). Sensitivity analyses using
22 the most recent theoretical predictions (Vereecken et al., 2015) indicate that the reaction with
23 ozone may be significant under certain conditions, accounting for up to 7% of SCI loss for
24 *anti*-SCI (based on *anti*-CH₃CHO) at the lowest RH (worst case) experiment. However,
25 generally SCI loss to ozone is calculated to be < 5% for *anti*-SCI and < 1% for *syn*-SCI.
26 Summed losses from reaction with SCI (self-reaction), carbonyls and alkenes are calculated to
27 account for < 1 % of the total SCI loss under the experimental conditions applied.

28 CH₂OO and CH₃CHOO have been shown to react rapidly ($k = 1 - 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) with
29 formic and acetic acid (Welz et al., 2014). In ozonolysis experiments, Sipilä et al. (2014)
30 determined the relative reaction rate of acetic and formic acids with (CH₃)₂COO (*i.e.* k_5/k_2) to
31 be roughly three. Organic acid mixing ratios in this work, as measured by FTIR, reached up to



1 a few hundreds of ppbv, suggesting these will likely be a significant SCI sink in our
2 experiments. We have therefore explicitly included reaction with organic acids in our
3 analysis, incorporating the uncertainty arising from the (unknown) acid reaction rate constant,
4 as described in Section 2.2.1.

5 To date, the effects of the water dimer, (H₂O)₂ on SCI removal have only been determined
6 experimentally for CH₂OO (Berndt et al., 2014; Chao et al., 2015; Lewis et al., 2015;
7 Newland et al., 2015a). Theoretical calculations (Vereecken and Francisco, 2012) predicted
8 the significant effect of the water dimer compared to the monomer for CH₂OO, but also that
9 the ratio of the SCI + (H₂O)₂ : SCI + H₂O rate constants, k_5/k_3 , of the larger, more substituted
10 SCI, *anti*-CH₃CHOO and (CH₃)₂COO, are 2 - 3 orders of magnitude smaller than for CH₂OO
11 (Vereecken and Francisco, 2012). This would make the dimer reaction negligible at
12 atmospherically accessible [H₂O] (*i.e.* $< 1 \times 10^{18} \text{ cm}^{-3}$) for SCI larger than CH₂OO. Therefore,
13 the effect of the water dimer reaction with C₁₀- and C₉-SCI is not considered in this analysis.
14 For CH₂OO, the reaction rates with water and the water dimer have been quantified in recent
15 EUPHORE experimental studies, and the values from Newland et al. (2015a) are used.

16 2.2.1 Derivation of $k(\text{SCI}+\text{H}_2\text{O})/k(\text{SCI}+\text{SO}_2)$ and $k_d/k(\text{SCI}+\text{SO}_2)$

17 As noted above, a range of different SCI are produced from the ozonolysis of the three
18 monoterpenes (see Schemes 2 – 4), each with their own distinct chemical behaviour, which
19 treated individually, introduce too many unknowns (*i.e.* yields, reaction rates) for explicit
20 analysis. Consequently for analytical purposes we treat the SCI population in a simplified
21 (lumped) manner:

22 Firstly, we use the simplest model possible, assuming that a single SCI is formed in each
23 ozonolysis reaction (Equation E3).

$$24 \quad \frac{f}{[\text{SO}_2]} = \left([\text{SO}_2] + \frac{k_3}{k_2} [\text{H}_2\text{O}] + \frac{k_d}{k_2} + \frac{k_5}{k_2} [\text{acid}] \right)^{-1} \quad (\text{E3})$$

25 Secondly, for each monoterpene, the SCI produced are assumed to belong to one of two
26 populations, denoted SCI-A and SCI-B. These two populations are split according to the
27 observation that the decomposition rates and reaction rates with water for the smaller SCI
28 (CH₃CHOO) have been predicted theoretically (Ryzhkov and Ariya, 2004; Kuwata et al.,
29 2010; Anglada et al., 2011) and shown experimentally (Taatjes et al., 2013; Sheps et al.,



1 2014; Newland et al., 2015a) to exhibit a strong dependence on the structure of the molecule.
 2 The *syn*-CH₃CHOO conformer, which has the terminal oxygen of the carbonyl oxide moiety
 3 in the *syn* position to the methyl group, has been shown to react very slowly with water and to
 4 readily decompose, via the hydroperoxide mechanism; whereas the *anti*-CH₃CHOO
 5 conformer, with the terminal oxygen of the carbonyl oxide moiety in the *anti*-position to the
 6 methyl group, has been shown to react fast with water and is not able to decompose via the
 7 hydroperoxide mechanism. Vereecken and Francisco (2012) have shown that all SCI studied
 8 theoretically with an alkyl group in the *syn* position have reaction rates with H₂O of $k < 4 \times$
 9 10^{-17} molecule cm³ s⁻¹ (and for SCI larger than acetone oxide, $k < 8 \times 10^{-18}$ molecule cm³ s⁻¹).

10 We thus define two populations, assuming SCI-A (i.e. SCI that exhibit chemical properties of
 11 the *anti*-type SCI) to react fast with water and not to undergo unimolecular reactions, and
 12 SCI-B (i.e. SCI that exhibit chemical properties of the *syn* type SCI) to not react with water
 13 but to undergo unimolecular reactions. This simplification allows us to fit to the
 14 measurements using Equations E4 and E5, as shown below. The total SCI yields are
 15 determined by our experiments at high SO₂, and the relative yields of SCI-A and SCI-B are
 16 determined from fitting to Equation E5. These relative yields are then compared to those
 17 predicted from the literature.

18 In this model, $f = \gamma^A f^A + \gamma^B f^B$, where γ is the fraction of the total SCI yield (i.e. $\gamma^A + \gamma^B = 1$). f^A
 19 and f^B are the fractional losses of SCI-A and SCI-B to reaction with SO₂. Adapting Equation
 20 E1 to include the two SCI species gives Equation E4, where $k_5[\text{acid}]$ accounts for the SCI +
 21 acid reaction (see discussion of reaction rate constants below).

$$22 \quad f = \frac{\gamma^A k_2^A [\text{SO}_2]}{k_2^A [\text{SO}_2] + k_3 [\text{H}_2\text{O}] + k_5^A [\text{acid}]} + \frac{\gamma^B k_2^B [\text{SO}_2]}{k_2^B [\text{SO}_2] + k_d + k_5^B [\text{acid}]} \quad (\text{E4})$$

23 Equation E4 can be rearranged to Equation E5 and fitted according to $f/[\text{SO}_2]$ derived from
 24 the measurements.

$$25 \quad \frac{f}{[\text{SO}_2]} = \frac{\gamma^A}{[\text{SO}_2] + \frac{k_3}{k_2^A} [\text{H}_2\text{O}] + \frac{k_5^A}{k_2^A} [\text{acid}]} + \frac{\gamma^B}{[\text{SO}_2] + \frac{k_d}{k_2^B} + \frac{k_5^B}{k_2^B} [\text{acid}]} \quad (\text{E5})$$

26 Using values for γ^A and γ^B from the literature and varying the assumed values of the reaction
 27 of SCI with acid (k_5) allows us to determine k_3/k_2^A and k_d/k_2^B .



1 The assumptions made here allow analysis of a very complex system. However, a key
2 consequence is that the relative rate constants obtained from the analysis presented here are
3 not representative of the elementary reactions of any single specific SCI isomer formed, but
4 rather represent a quantitative ensemble description of the integrated system, under
5 atmospheric boundary layer conditions, which may be appropriate for atmospheric modelling.
6 Additionally our experimental approach cannot determine absolute rate constants (*i.e.* values
7 of k_2 , k_3 , k_d) in isolation, but is limited to assessing their relative values, measured under
8 atmospheric conditions, which may be placed on an absolute basis through use of an external
9 reference value (here the SCI + SO₂ rate constant).

10 2.2.2 SCI yield calculation

11 The value for the total SCI yield of each monoterpene, $\phi_{\text{SCI-TOT}}$, was determined from an
12 experiment performed under dry conditions (RH < 1%) in the presence of excess SO₂ (*ca.*
13 1000 ppbv), such that SO₂ scavenged the majority of the SCI. From Equation E2, regressing
14 $d\text{SO}_2$ against $d\text{O}_3$ (corrected for chamber dilution), assuming f to be unity (*i.e.* all the SCI
15 produced reacts with SO₂), determines the value of ϕ_{min} , a lower limit to the SCI yield. Figure
16 1 shows the experimental data, from which ϕ_{min} was derived.

17 In reality f will be less than one, at experimentally accessible SO₂ levels, as a fraction of the
18 SCI may still react with trace H₂O present, or undergo unimolecular reaction. The actual
19 yield, ϕ_{SCI} , was determined by combining the result from the excess-SO₂ experiment with
20 those from the series of experiments performed at lower SO₂, as a function of [H₂O], to obtain
21 k_3/k_2 and k_d/k_2 (see Section 2.2.1), through an iterative process to determine the single unique
22 value of ϕ_{SCI} which fits both datasets, as described in Newland et al. (2015a), but taking into
23 account the proposed model in this paper of there being two SCI produced. In this model, $f =$
24 $\gamma^A f^A + \gamma^B f^B$. Where $f^A = [\text{SO}_2] / ([\text{SO}_2] + k_3[\text{H}_2\text{O}]/k_2)$ and $f^B = [\text{SO}_2] / ([\text{SO}_2] + k_d/k_2)$ – other
25 possible SCI sinks are assumed to be negligible. In these excess-SO₂ experiments, $f^A \sim 1$ but
26 $f^B < 1$ since k_d still represents a significant sink.

27 γ^A (and hence γ^B , since $\gamma^B = 1 - \gamma^A$) is derived from fitting Equation E4 to the data from the
28 experiments performed at lower SO₂ for a given ϕ . Using a range of ϕ , gives a range of γ .
29 These different values of γ are used with the respective values of ϕ in fitting to Equation E4
30 to determine values of k_3/k_2 and k_d/k_2 .

31



1 3 Theoretical calculations

2 The rovibrational characteristics of all conformers of the CI formed from α -pinene and β -
3 pinene, the transition states for their unimolecular reaction, and for their reaction with H_2O ,
4 were characterized quantum chemically, first using the M06-2X/cc-pVDZ level of theory, and
5 subsequently refined at the M06-2X/aug-cc-pVTZ level. To obtain accurate barrier heights for
6 reaction, it has been shown (Berndt et al., 2015; Chhantyal-Pun et al., 2017; Fang et al.,
7 2016a, 2016b; Long et al., 2016; Nguyen et al., 2015) that post-CCSD(T) calculations are
8 necessary. Unfortunately, performing such calculations for the SCI discussed in this paper,
9 with up to 14 non-hydrogen atoms, is well outside our computational resources, though
10 CCSD(T)/aug-cc-pVTZ single point energy calculations were performed for the unimolecular
11 reactions of nopinone oxides and the most relevant subset of pinonaldehyde oxides. These
12 data are sufficient for relative rate estimates, but it remains useful to improve the absolute
13 barrier height predictions, using the data set by Vereecken et al. (Vereecken et al., 2017). This
14 data set has a large number of systematic calculations on smaller CI, allowing empirical
15 corrections to the DFT or CCSD(T) barrier heights to estimate the post-CCSD(T) barrier
16 heights. The methodology for these corrections is described in more detail in Vereecken et al.
17 (2017); briefly, it compares rate coefficient calculations against available harmonized
18 experimental and very-high level theoretical kinetic rate predictions, and adjusts the barrier
19 heights by 0.4 to 2.6 kcal mol⁻¹ (depending on the base methodology and the reaction type) to
20 obtain best agreement with these benchmark results.

21 Using the energetic and rovibrational data thus obtained, multi-conformer transition state
22 theory (MC-TST) calculations (Truhlar et al., 1996; Vereecken and Peeters, 2003) were
23 performed to obtain the rate coefficient at 298K at the high pressure limit. All rate predictions
24 incorporate tunnelling corrections using an asymmetric Eckart barrier (Eckart, 1930; Johnston
25 and Heicklen, 1962). For the reaction of CI + H_2O , a pre-reactive complex is postulated at 7
26 kcal mol⁻¹ below the free reactants, while the CI + (H_2O)₂ reaction is taken to have a pre-
27 reactive complex of 11 kcal mol⁻¹ stability. This pre-reactive complex affects tunnelling
28 corrections; it is assumed that this pre-reactive complex is always in equilibrium with the free
29 reactants.

30 In view of the high number of rotamers and the resulting computational cost, only a single
31 limonene-derived CI isomer was studied, where the TS for the CI + H_2O reaction was
32 analyzed at the M06-2X/cc-pVDZ level of theory with only a partial conformational analysis;



1 a limited number of the energetically most stable TS conformers thus discovered were re-
2 optimized at the M06-2X/aug-cc-pVTZ level of theory. These data will only be used for
3 qualitative assessments. However, we apply the structure-activity relationships (SARs)
4 presented by Vereecken et al. (Vereecken et al., 2017) to obtain an estimate of the rate
5 coefficients, and assess the role of the individual SCI isomers in limonene ozonolysis.

6 All quantum chemical calculations were performed using Gaussian-09 (Frisch et al., 2010).

7

8 **4 GEOS-Chem Model Simulation**

9 The global chemical transport model GEOS-Chem (v9-02, www.geos-chem.org, Bey et al.,
10 2002) is used to explore the spatial and temporal variability of the atmospheric impacts of the
11 experimentally derived chemistry. The model includes HO_x-NO_x-VOC-O₃-BrO_x chemistry
12 (Mao et al., 2010; Parrella et al., 2012) and a mass-based aerosol scheme. Biogenic
13 monoterpene emissions are taken from the Model of Emissions of Gases and Aerosols from
14 Nature (MEGAN) v2.1 inventory (Guenther et al., 2006; 2012). Transport is driven by
15 assimilated meteorology (GEOS-5) from NASA's Global Modelling and Assimilation Office
16 (GMAO). The model is run at 4°×5° resolution, with the second year (2005) used for analysis
17 and first year discarded as spin up.

18 In this study, the standard simulation was expanded to include emissions of seven
19 monoterpene species (α -pinene, β -pinene, limonene, myrcene, ocimene, carene, and sabinene)
20 from MEGAN v2.1. The ozonolysis scheme for each monoterpene, detailed in Section 6.1,
21 considers the formation of one or two types of SCI, and their subsequent reaction with SO₂,
22 H₂O, or unimolecular decomposition. Reaction rate of the monoterpenes with OH, O₃ and
23 NO₃ rare detailed in Table S1.

24

25 **5 Results**

26 **5.1 SCI Yield**

27 Figure 1 shows the lower limit to the SCI yield, ϕ_{\min} , for the three monoterpenes, determined
28 from fitting Equation E5 to the experimental data. This gives values of 0.16 (\pm 0.01) for α -
29 pinene, 0.53 (\pm 0.01) for β -pinene and 0.20 (\pm 0.01) for limonene. These ϕ_{\min} values were
30 then corrected as described in Section 2.2.2 using the k_3/k_2 and k_d/k_2 values determined from



1 the measurements shown in Figures 3 – 5 using Equation E4. The corrected yields, ϕ_{SCI} , are
2 0.19 (± 0.01) for α -pinene, 0.60 (± 0.03) for β -pinene and 0.23 (± 0.01) for limonene.
3 Uncertainties are $\pm 2\sigma$, and represent the combined systematic (estimated measurement
4 uncertainty) and precision components. Literature yields for SCI production from
5 monoterpene ozonolysis are summarised in Table 1.

6 The value derived for the total SCI yield from α -pinene in this work of 0.19 agrees, within the
7 uncertainties, with the value of 0.15 (± 0.07) reported by Sipilä et al. (2014) and the value of
8 0.20 applied in the MCMv3.3.1.

9 The total SCI yield from β -pinene derived in this work, 0.60, agrees reasonably well with the
10 recent experimental work of Ahrens et al. (2014) who derived a total SCI yield of 0.50 (0.40
11 for the sum of CI-1 and CI-2 and 0.10 for CH_2OO , which is assumed to be formed almost
12 completely stabilised). The MCMv3.3.1 applies a total SCI yield of 0.25, of which 0.10 is a
13 C9-CI and 0.15 is CH_2OO . Earlier studies also tended to derive lower total SCI yields ranging
14 from 0.25 – 0.27 (Hasson et al., 2001; Hatakeyama et al., 1984).

15 The total SCI yield from limonene derived in this work, 0.23 (± 0.01) agrees with the recently
16 determined yield from Sipilä et al. (2014) of 0.27 (± 0.12). Leungsakul et al. (2005) derived a
17 somewhat higher yield of 0.34, while the MCMv3.3.1 applies a lower yield of 0.135.

18 **5.2 $k_3(\text{SCI}+\text{H}_2\text{O})/k_2(\text{SCI}+\text{SO}_2)$ and $k_d/k_2(\text{SCI}+\text{SO}_2)$ Analysis**

19 Figure 2 shows the loss of SO_2 as ozone is consumed by reaction with the monoterpene for
20 each of the three systems. Box modelling results suggest that $> 99\%$ of this SO_2 removal is
21 caused by reaction with SCI produced in the alkene-ozone reaction (rather than e.g. reaction
22 with OH, which is scavenged by cyclohexane). When the experiments are repeated at higher
23 relative humidity, the rate of loss of SO_2 decreases. This is as expected from Equation E1 and
24 suggests that there is competition between SO_2 and H_2O for reaction with the SCI produced,
25 in agreement with observations of smaller SCI, which demonstrate the same competition
26 under atmospherically relevant conditions (Newland et al., 2015a; Newland et al., 2015b).

27 However, as the relative humidity is increased further, the SO_2 loss does not fall to (near) zero
28 as would be expected from Equation E1. This suggests that at high $[\text{H}_2\text{O}]$ the amount of SO_2
29 loss becomes less sensitive to $[\text{H}_2\text{O}]$. This is most likely due to there being at least two
30 chemically distinct SCI species present. This behaviour was previously observed for



1 CH₃CHOO by Newland et al. (2015a) and fits with the current understanding that the
2 reactivity of SCI is structure dependent.

3 To recap Section 2.2.1, the analysis presented here considers two models to fit the
4 observations. The first of these (Equation E3) assumes the formation of a single SCI species,
5 which, in addition to reacting with SO₂, can react with water, undergo unimolecular reaction
6 or react with acid. It is clearly evident from Figures 3 – 5 that this model does not give a good
7 fit to the observations for any of the monoterpene systems studied. Therefore, the results from
8 this (single SCI) approach are not discussed explicitly hereafter. The second of the models
9 (Equation E5) assumes the formation of two lumped, chemically distinct, populations of SCI,
10 denoted SCI-A and SCI-B. SCI-A is assumed to react fast with H₂O and to have minimal
11 decomposition. Conversely, SCI-B is assumed to have a negligible reaction with water under
12 the experimental conditions applied but to undergo rearrangement via a VHP. We use a least-
13 squares fit of Equation E5 to the data to determine the values of k_3/k_2 and k_d/k_2 . This approach
14 fits the data well (Figures 3 - 5) for all 3 monoterpenes and represents the overall attributes of
15 the SCI formed - but as noted, does not represent an explicit determination of individual
16 conformer-dependent rate constants.

17 5.2.1 α -pinene

18 The α -pinene system is sensitive to water vapour at the low H₂O range, with the SO₂ loss
19 falling dramatically when the RH is increased from 0.1 to 2.5 % (Figure 2). However, at
20 higher RH the SO₂ loss appears to be rather insensitive to [H₂O].

21 CI-1 can be formed in either a *syn* (1a) or *anti* (1b) configuration, whereas both CI-2
22 conformers formed are in a *syn* configuration (see Scheme 2). For one of the two conformers
23 of CI-2 (CI-2b), the hydrogen atom available for abstraction by the terminal oxygen of the
24 carbonyl oxide group is attached to the carbon on the four-membered ring. This has been
25 shown in the β -pinene system to make a large difference with respect to the ability of the
26 hydrogen to be abstracted and to undergo the VHP mechanism (Rickard et al., 1999; Nguyen
27 et al., 2009). This therefore suggests that CI-2b may exhibit characteristics of both SCI-A and
28 SCI-B. Ma et al. (2008) infer a probable equal yield of the two basic CI structures. This
29 would suggest a relative yield for SCI-A of 0.25 – 0.50 (depending on the precise nature of
30 CI-2b). Fitting Equation E4 to the data and allowing λ to vary determines values of $\gamma^A =$
31 0.40 and $\gamma^B = 0.60$ (Figure 3).



1 In Figure 3, Equation E4 is fitted to the α -pinene measurements, assuming
2 $k(\text{SCI+acid})/k(\text{SCI+SO}_2) = 0$. This derives a minimum value for $k(\text{SCI-A+H}_2\text{O})/k(\text{SCI-}$
3 $\text{A+SO}_2)$, the water dependent fraction of the SCI, and a maximum value for
4 $k(\text{decomposition:SCI-B})/k(\text{SCI-B+SO}_2)$, the water independent fraction of the SCI. The
5 kinetic parameters derived from the fitting are displayed in Table 2.

6 Figure 6 shows the variation of the derived k_3/k_2 and k_d/k_2 values as the ratio k_5/k_2 ,
7 $k(\text{SCI+acid})/k(\text{SCI+SO}_2)$, is varied from zero to one. The derived k_3/k_2 increases by about 40
8 % from $1.4 (\pm 0.34) \times 10^{-3}$ to $2.0 (\pm 0.49) \times 10^{-3}$. The derived k_d/k_2 value decreases, again by
9 about 40 %, from $8.2 (\pm 1.5) \times 10^{12} \text{ cm}^{-3}$ to $5.1 (\pm 0.93) \times 10^{12} \text{ cm}^{-3}$.

10 The derived limits to the relative rate constants can be put on an absolute scale using the
11 $k(\text{SCI+SO}_2)$ values for CH_3CHOO from Sheps et al. (2014) for the *syn* and *anti* conformers.
12 These are, *syn*: $2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and *anti*: $2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The *syn* rate constant is applied
13 to the derived $k(\text{decomposition:SCI-B})/k(\text{SCI-B+SO}_2)$ value and the *anti* rate constant to the
14 $k(\text{SCI-A+H}_2\text{O})/k(\text{SCI-A+SO}_2)$ value. It should be noted that the k_2 values are for quite
15 different SCI to those formed in this study and to our knowledge no structure specific
16 $k(\text{SCI+SO}_2)$ have been reported for monoterpene derived SCI, though Ahrens et al. (2014)
17 determine an average $k_2 \sim 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for SCI derived from β -pinene, i.e. a value within
18 an order of magnitude of those determined for the smaller SCI CH_2OO , CH_3CHOO and
19 $(\text{CH}_3)_2\text{COO}$ (e.g. Welz et al., 2012; Taatjes et al., 2013; Sheps et al., 2014; Huang et al.,
20 2015). Using the Sheps et al. (2014) values yields $k(\text{SCI-A+H}_2\text{O}) > 3.1 (\pm 0.75) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
21 and $k(\text{decomposition:SCI-B}) < 240 (\pm 44) \text{ s}^{-1}$ (using the values derived for $k(\text{SCI-}$
22 $\text{A+acid})/k(\text{SCI-A+SO}_2) = 0$). This k_3 value is an order of magnitude larger than the rate
23 constants determined for the smaller *anti*- CH_3CHOO in the direct studies of Sheps et al.
24 (2014) ($2.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$) and Taatjes et al. (2013) ($1.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$). The decomposition
25 value derived for SCI-B is of the same order of magnitude as that for *syn*- CH_3CHOO ($348 \pm$
26 332 s^{-1}) and $(\text{CH}_3)_2\text{COO}$ ($819 \pm 190 \text{ s}^{-1}$) from Newland et al., (2015a) (using updated direct
27 measurement values of k_2 from Sheps et al. (2014) and Huang et al. (2015) for *syn*-
28 CH_3CHOO and $(\text{CH}_3)_2\text{COO}$ respectively) and within the range from the recent paper by
29 Smith et al. (2016) which derives a decomposition rate for $(\text{CH}_3)_2\text{COO}$ of $269 (\pm 82) \text{ s}^{-1}$ at
30 283 K increasing to $916 (\pm 56) \text{ s}^{-1}$ at 323 K.

31 Sipilä et al. (2014) applied a single-SCI analysis approach to the formation of H_2SO_4 from
32 SO_2 oxidation in the presence of the α -pinene ozonolysis system. They determined that for α -



1 pinene, $k_d \gg k(\text{SCI}+\text{H}_2\text{O})[\text{H}_2\text{O}]$ for $[\text{H}_2\text{O}] < 2.9 \times 10^{17} \text{ cm}^{-3}$, i.e. that the fate of SCI formed
2 in the system is rather insensitive to $[\text{H}_2\text{O}]$. Across the $[\text{SO}_2]$ and RH ranges used in their
3 study, the results obtained here would indicate H_2O to always be the dominant sink for SCI-
4 A, i.e. the fact that Sipilä et al. (2014) see similar H_2SO_4 production across the RH range in
5 their study is consistent with these results.

6

7 5.2.2 β -pinene

8 Two recent studies (Nguyen et al., 2009; Ahrens et al., 2014) have suggested yields of the two
9 C_9 -CI (CI-3 and CI-4, see Scheme 3) obtained from β -pinene ozonolysis to be roughly equal.
10 In these studies Ahrens et al. (2014) assume a CH_2OO yield of 0.10 while Nguyen et al.
11 (2009) determine theoretically the yield of CH_2OO to be 0.05. Another theoretical study
12 (Zhang and Zhang, 2005) predicted a CH_2OO yield of 0.08. In experimental studies,
13 Winterhalter et al. (2000) determined the CH_2OO yield to be 0.16 (± 0.04) from measuring
14 the nopinone yield and assuming it to be entirely a primary ozonolysis product (i.e. the co-
15 product of CH_2OO formation) and Ma and Marston (2008) determine a summed contribution
16 of 84 % (± 0.03) for the two C_9 -CI (i.e. a 16 % CH_2OO yield). The theoretical studies are
17 somewhat lower than the experimental but Nguyen et al. (2009) note that CI-4 is likely to
18 form additional nopinone in bimolecular reactions. The CH_2OO is assumed to all be formed
19 stabilised (e.g. Nguyen et al. 2009).

20 SCI-3 is expected to undergo unimolecular reactions at least an order of magnitude faster than
21 SCI-4 (Nguyen et al., 2009; Ahrens et al., 2014). The reaction of SCI-3 with water is expected
22 to be slow based on the calculations presented in Table 4, with a pseudo first order reaction
23 rate of 1.0 s^{-1} at 75 % RH, 298 K, whereas the water reaction with SCI-4 is expected to be
24 considerably faster with a pseudo first order reaction rate of 240 s^{-1} at 75 % RH, 298 K. This
25 reaction will thus likely be the dominant fate of SCI-4 at typical atmospheric RH. This is in
26 agreement with the observations of Ma and Marston (2008), that show a clear dependence of
27 nopinone formation on RH (presumed to be formed from $\text{SCI} + \text{H}_2\text{O}$). Fitting Equation E4 to
28 the data determines values of $\gamma^A = 0.41$ and $\gamma^B = 0.59$ (Figure 4).

29 Using these values, and assuming $k(\text{SCI}+\text{acid})/k(\text{SCI}+\text{SO}_2) = 0$, yields a $k(\text{SCI}-$
30 $\text{A}+\text{H}_2\text{O})/k(\text{SCI}-\text{A}+\text{SO}_2)$ value of $> 1.0 (\pm 0.27) \times 10^{-4}$ and a $k(\text{decomposition:SCI-B})/k(\text{SCI}-$
31 $\text{B}+\text{SO}_2)$ value of $< 6.0 (\pm 1.3) \times 10^{12} \text{ cm}^{-3}$ (Table 2).



1 As shown in Figure 6, increasing k_5/k_2 , $k(\text{SCI+acid})/k(\text{SCI+SO}_2)$, from zero to one, decreases
2 the derived k_d/k_2 from $6.0 (\pm 1.3) \times 10^{12} \text{ cm}^{-3}$ to $1.8 (\pm 0.39) \times 10^{12} \text{ cm}^{-3}$. The derived k_3/k_2
3 increases by a factor of four from $1.0 (\pm 0.27) \times 10^{-4}$ to $3.7 (\pm 1.0) \times 10^{-4}$.

4 These values can be put on an absolute scale (using the values derived above for $k_5/k_2 = 0$).
5 For SCI-A, $k(\text{SCI+SO}_2)$ is taken as the experimentally determined value of $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
6 from Ahrens et al. (2014). For SCI-B, the *syn*-CH₃CHOO $k(\text{SCI+SO}_2)$ value determined by
7 Sheps et al. (2014) is used. This gives values of $k(\text{SCI-A+H}_2\text{O}) > 4 \times 10^{-15} (\pm 1) \text{ cm}^3 \text{ s}^{-1}$ and
8 $k(\text{decomposition:SCI-B}) < 170 (\pm 38) \text{ s}^{-1}$.

9 5.2.3 Limonene

10 For the limonene measurements presented in Figure 2, $(d\text{SO}_2/d\text{O}_3)/dt$ appears to be non-
11 linear, with a jump in $d\text{SO}_2/d\text{O}_3$ between 120 and 150 ppbv of ozone consumed. This is most
12 evident in the two lowest RH runs (0.2 and 2.0 %). Limonene is the fastest reacting of the
13 systems presented here, with the alkene reaction having consumed 100 ppbv of ozone within
14 the first five minutes. The limonene sample required about five minutes of heating before the
15 entire sample was volatilized and injected into the chamber. This therefore may account for the
16 apparent non-linear nature of $d\text{SO}_2/d\text{O}_3$ in Figure 2.

17 The SO₂ loss in the limonene-ozone system is less affected by increasing H₂O than for either
18 α or β -pinene (Figure 5), with the values of $f/[\text{SO}_2]$ (y-axis) varying by roughly a factor of two
19 over the RH range applied compared to more than a factor of three variation for the other two
20 systems. Hence it might be expected that there is little formation of H₂O dependent SCI or
21 that it has a rather slow reaction rate with water.

22 Fitting Equation E4 to the data determines values of $\gamma^A = 0.22$ and $\gamma^B = 0.78$ (Figure 5). This
23 is broadly in line with the ratio recommended in the MCMv3.3.1 of 0.27:0.73, and with that
24 proposed in Leungsakul et al. (2005) who use a CI-A:CI-B ratio of 0.35:0.65, but also include
25 some stabilisation of CH₂OO and C₉-CI from ozone reaction at the exo-cyclic bond. This
26 yields a $k(\text{SCI-A+H}_2\text{O})/k(\text{SCI-A+SO}_2)$ value of $< 3.5 (\pm 0.20) \times 10^{-5}$ and a
27 $k(\text{decomposition:SCI-B})/k(\text{SCI-B+SO}_2)$ value of $> 4.5 (\pm 0.10) \times 10^{12} \text{ cm}^{-3}$.

28 Figure 6 shows that the derived k_d/k_2 increases by about 7 % as $k(\text{SCI+acid})/k(\text{SCI+SO}_2)$
29 ranges from 0.0 to 0.8. The derived k_3/k_2 becomes negative at $k(\text{SCI+acid})/k(\text{SCI+SO}_2) > 0.8$,
30 putting an upper limit on this ratio, i.e. $k_5/k_2 < 0.8$, for the limonene system.



1 Putting these values on an absolute scale (using the values derived for $k_3/k_2 = 0$), using the
2 CH_3CHOO *syn* and *anti* $k(\text{SCI}+\text{SO}_2)$ determined by Sheps et al. (2014), yields values of < 7.7
3 $(\pm 0.60) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and $> 130 (\pm 3) \text{ s}^{-1}$ for k_3 and k_d respectively. These values are similar
4 to those derived for the SCI-A and SCI-B formed from β -pinene. The k_3 value is a factor of
5 three smaller than that determined by Sheps et al. (2014) for $k_3(\text{anti-CH}_3\text{CHOO}+\text{H}_2\text{O})$, $2.4 \times$
6 $10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

7 Sipilä et al. (2014) applied a single-SCI analysis approach to the formation of H_2SO_4 from
8 SO_2 oxidation by the limonene ozonolysis system and determined that, similarly to α -pinene,
9 $k(\text{decomp.}) \gg k(\text{SCI}+\text{H}_2\text{O})[\text{H}_2\text{O}]$ for $[\text{H}_2\text{O}] < 2.9 \times 10^{17} \text{ cm}^{-3}$, i.e. that the system is rather
10 insensitive to $[\text{H}_2\text{O}]$. Our data are consistent with the limonene system being less sensitive to
11 $[\text{H}_2\text{O}]$ than the SCI populations derived from the other two monoterpenes reported here.

12 5.2.4 Experimental Summary

13 The removal of SO_2 in the presence of ozonolysis reactions of α -pinene, β -pinene and
14 limonene has been studied as a function of water vapour concentration, and analysed
15 following the approximation that the SCI population can be represented through a two species
16 model, with contrasting unimolecular decomposition rates and reactivity to water. The results
17 presented in this work suggest that all three monoterpenes studied produce a range of SCI that
18 have differing reactivities towards water and decomposition. This is in agreement with current
19 theoretical understanding but is the first experimental demonstration for large SCI derived
20 from monoterpene ozonolysis. The complex reactivity of the systems investigated is further
21 highlighted by the fact that the experimental data are not fitted well by the assumption of the
22 formation of a single SCI species. While the behaviour of large SCI derived from
23 monoterpenes are likely to be significantly more complicated than is accounted for by simply
24 considering the differing kinetics of *syn* and *anti* SCI conformers, this approach provides a
25 reasonable description of the experimental behaviour observed, and the results presented here
26 are broadly in line with experimental results from the smaller SCI and from theoretical
27 results. The reaction rates of SCI-A (i.e. SCI that exhibit chemical properties of the *anti*-type
28 SCI) derived from the three different monoterpenes with water range from < 0.8 to $> 31 \times 10^{-}$
29 $14 \text{ cm}^3 \text{ s}^{-1}$, broadly in line with the derived rates of Sheps et al. (2014) for *anti-CH}_3\text{CHOO} of
30 $2.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. The decomposition rates of SCI-B (i.e. SCI that exhibit chemical
31 properties of the *syn*-type SCI) are on the order of $100 - 250 \text{ s}^{-1}$. This is in line with those
32 derived for *syn-CH}_3\text{CHOO} from *cis* and *trans*-but-2-ene ozonolysis and $(\text{CH}_3)_2\text{COO}$ by**



1 Newland et al. (2015a) of $348 (\pm 332) \text{ s}^{-1}$ and $819 (\pm 190) \text{ s}^{-1}$ respectively (assuming $k(\text{syn-}$
2 $\text{CH}_3\text{CHOO}+\text{SO}_2) = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Sheps et al., 2014) and $k((\text{CH}_3)_2\text{COO}+\text{SO}_2) = 2.9 \times$
3 $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Huang et al., 2015)) and recent results from Smith et al. (2016) of $269 - 916 \text{ s}^{-1}$
4 (strongly dependent on temperature) for $(\text{CH}_3)_2\text{COO}$ decomposition. In this work we only
5 derive relative rates, but the similarity of the k_3 and k_d values derived when the k_2 values for
6 *syn* and *anti*- CH_3CHOO from Sheps et al. (2014) are applied is consistent with the recent
7 work of Ahrens et al. (2014), suggesting that large SCI, derived from monoterpenes,
8 demonstrate a similar reactivity towards SO_2 as smaller SCI. One uncertainty in the derivation
9 of the kinetics presented herein is the reactions of the SCI produced with organic acids. These
10 acids were present in the experiments (owing to formation in the monoterpene ozonolysis
11 reactions themselves) at levels which may have been a competitive sink for the SCI.

12 The ability of the simplified SCI-A / SCI-B approach to fit the experimental data and the
13 good agreement with theory and experimental work for smaller SCI suggests that the kinetic
14 parameters derived herein, using a lumped two-SCI system, may be useful for modelling and
15 provide the best available basis for modelling the effects of SCI on atmospheric SO_2
16 oxidation in the presence of water vapour. To this end, in Section 6 we present the results of a
17 global modelling study using the kinetic parameters derived herein.

18 **5.3 Theoretical results and comparison to experiments**

19 The theoretically predicted rate coefficients for unimolecular reactions of the monoterpene
20 SCI are listed in Table 3, while those for the reaction with H_2O are listed in Table 4. These
21 data can be compared against the experimental data obtained in this work.

22 **5.3.1 α -pinene**

23 The theory-based rate coefficients show one pinonaldehyde oxide, CI-1b, with a rate of
24 reaction with water that is significantly faster than the remaining α -pinene-derived CI.
25 Comparing this rate to the experimental data suggests that CI-1b corresponds to SCI-A, with
26 matching rate coefficients within an order of magnitude, i.e. within the expected uncertainty.
27 We thus deduce that SCI-A is CI-1b. The remaining pinonaldehyde oxides, CI-1a, CI-2a and
28 CI-2b, react predominantly through unimolecular reactions, where theory-based rate
29 coefficients range from 60 to 600 s^{-1} , all within a factor of 4 of the experimentally derived
30 population-averaged rate of $240 \pm 44 \text{ s}^{-1}$, i.e. matching within the uncertainty margins. The



1 unimolecular rate coefficients of this set of CI are sufficiently close that it is not feasible to
2 separate these in the experimental data, so we can only conclude that SCI-B in the α -pinene
3 ozonolysis experiments may consist of a mixture of C-1a, CI-2a and CI-2b.

4 5.3.2 β -pinene

5 The theoretical analysis for nopinone oxides shows one isomer, SCI-4, that has a fast rate of
6 reaction with water, but a slow unimolecular isomerisation, while the other isomer, SCI-3,
7 shows a fast unimolecular decomposition. These can thus be unequivocally equated to the
8 experimentally obtained SCI-A and SCI-B, respectively, inasmuch as the yield of CH₂OO is
9 minor. The predicted rate coefficients are within the expected uncertainty intervals of the
10 theoretical data, a factor of 5 for the unimolecular rates, and an order of magnitude for the
11 reaction with H₂O.

12 The experimental rate measurements are defined relative to the reaction rate with SO₂; the
13 value adopted for the $k(\text{SCI}+\text{SO}_2)$ reaction therefore influences the derived rate coefficient
14 values. Ahrens et al. (2014) directly measured the SO₂ rate coefficient of the longest-lived
15 SCI (SCI-4) to be $\sim 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, but for SCI-3 we assume a similar rate coefficient as
16 *syn*-CH₃CHOO + SO₂ determined by Sheps et al. (2014) of $2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Nopinone
17 oxides are bicyclic compounds, with a bulky dimethyl-substituted 4-membered ring adjacent
18 to the carbonyl oxide moiety. To examine the potential impact of steric hindrance on the SCI
19 + SO₂ reaction, we characterized all sulfur-substituted secondary ozonides (S-SOZ) formed in
20 this reaction (Kuwata et al., 2015; Vereecken et al., 2012). We find that the tri-cyclic S-SOZ
21 shows very little interaction between the sulfur-bearing ring and the β -pinene substituents,
22 and little change in ring strain. The energies of the S-SOZ adducts relative to the SCI + SO₂
23 reactants thus remains very similar to that of CH₂OO, CH₃CHOO or (CH₃)₂COO, confirming
24 the quality of our selection of reference rate coefficients.

25 5.3.3 Limonene

26 Of the six non-CH₂OO CI formed in limonene ozonolysis, CI-5b was predicted to have a fast
27 reaction rate with H₂O; its oxide substitution patterns is similar to pinonaldehyde oxide CI-1b.
28 The SAR-predicted rate coefficient of CI-5b + H₂O is within a factor of 2 of the
29 experimentally derived k_3 value for SCI-A, such that we can equate SCI-A to CI-5b with
30 confidence. The SCI-B set of Criegee intermediates then contains the summed population of
31 the remaining five CI, all of which react slowly with H₂O. The SAR-predicted unimolecular



1 decay rate coefficients range from 15 to 700 s⁻¹, all within a factor of 9 of the experimentally
2 obtained $k_d = 130 \text{ s}^{-1}$; it should be noted that for limonene-derived CI, no explicit theoretical
3 calculations are available, and the SAR-predictions carry a somewhat larger uncertainty.
4 We have performed an exhaustive characterisation of the conformers of CI-5b. The most
5 stable conformers show an internal complex formation between the oxide moiety and the
6 carbonyl group, similar to those characterized for the bimolecular reaction of CI with
7 carbonyl compounds (Jalan et al., 2013; Wei et al., 2015). The theoretical study by Jiang et al.
8 (2013) on limonene ozonolysis appears to have omitted internal rotation and cannot be
9 compared directly. It seems likely that the limonene-derived CI can thus easily undergo
10 internal SOZ formation, which is thought (Vereecken and Francisco, 2012) to be entropically
11 unfavourable, but to have a low barrier to reaction. For α -pinene, a similar internal complex
12 formation and SOZ ring closure is not as favourable due to the geometric limitations enforced
13 by the 4-membered ring.

14 A large number of transition state conformers for CI-5b + H₂O were characterized, though no
15 exhaustive search was completed. The energetically most favourable structures show
16 interaction between the carbonyl group, and the H₂O co-reactant as it adds onto the carbonyl
17 oxide moiety. Similar stabilising interactions between the carbonyl moiety and the
18 carbonyl oxide moiety were reported recently in cyclohexene-derived CI
19 (Berndt et al., 2017). This interaction thus lowers the barrier to reaction though it is currently
20 unclear whether it enhances the reaction rate compared to e.g. the α -pinene-derived CI-1b, as
21 these hydrogen-bonded structures are entropically not very favourable. The intra-molecular
22 interactions with heterosubstituents could be investigated in future work.

23

24 **6 Global modelling study**

25 **6.1 SCI Chemistry**

26 A global atmospheric modelling study was performed using the GEOS-Chem chemical
27 transport model (as described in Section 4) to examine the global monoterpene derived SCI
28 budget and the contribution of these SCI to gas-phase SO₂ oxidation. The existing chemistry
29 scheme in the model is supplemented with monoterpene SCI chemistry based on the
30 experimental results described in Section 5 and in Table 5. It should be noted here that this
31 modelling study focuses on the chemical impacts of monoterpene SCI formed from



1 ozonolysis reactions only. No chemistry for other SCIs derived from isoprene and/or other
2 (smaller) alkenes are incorporated in the adapted model chemical scheme used.

3 The monoterpene emissions in GEOS-Chem are taken from MEGAN v2.1 (Guenther et al.,
4 2012). The scheme emits seven monoterpenes: α -pinene, β -pinene, limonene, myrcene,
5 ocimene, 3-carene, and sabinene. The monoterpenes are oxidised within the model by OH,
6 NO₃ and O₃ at rates shown in Table S1. Reaction with O₃ leads to the production of
7 monoterpene specific SCI. Reactions with OH and NO₃ does not lead to the formation of any
8 products, with the reactions only acting as a sink for the monoterpene and the respective
9 oxidant. The SCI yields from the ozonolysis of α -pinene, β -pinene, and limonene are derived
10 from the experimental work presented here. SCI from each monoterpene are split in to SCI-A
11 and SCI-B as defined in previous sections. For the other four monoterpenes emitted, the SCI
12 yields, and kinetics are derived based on similarity of structure to one of the species studied
13 here or previously in the literature. The main SCI produced in the ozonolysis of myrcene and
14 ocimene are expected to be acetone oxide ((CH₃)₂COO) or 4-vinyl-5-hexenal oxide
15 (CH₂CHC(CH₂)CH₂CH₂CHOO), since ozone has been suggested to react predominantly at
16 the isolated internal double bond (~97 % for myrcene, ~90% for ocimene (Baker et al.,
17 2004)). The SCI yield is taken to be 0.30, similar to that of (CH₃)₂COO from 2,3-dimethyl-
18 but-2-ene ozonolysis (Newland et al., 2015a). However, this may be an underestimate since it
19 has been predicted that stabilisation of small CI increases with an increasing size of carbonyl
20 co-product, as this co-product can take more of the nascent energy of the primary ozonide on
21 decomposition due to a greater number of degrees of freedom available (Nguyen et al., 2009,
22 Newland et al., 2015b). Sabinene is a bicyclic monoterpene with an external double bond and
23 hence is treated like β -pinene. This assumption is backed up by recent theoretical work (Wang
24 and Wang, 2017), who predict similar behaviour of sabinene derived SCI to the predicted
25 behaviour of β -pinene SCI by Nguyen et al. (2009a). They predict a SCI yield between 24 % -
26 64 %. 3-carene is a bicyclic monoterpene with an internal double bond and is treated like α -
27 pinene.

28 6.2 Modelling Results

29 Figure 7 shows the annually averaged total SCI burden from monoterpene ozonolysis in the
30 surface layer in the GEOS-Chem simulation. A number of interesting features are apparent
31 from this figure and the associated information given in Table 6:



1 (i) The highest annually averaged monoterpene SCI concentrations are found
2 above tropical forests.

3 (ii) Peak annually averaged monoterpene SCI concentrations are $\sim 1.2 \times 10^4 \text{ cm}^{-3}$.

4 (iii) $> 97 \%$ of the total monoterpene SCI burden is SCI-B.

5 Annual global monoterpene emissions are dominated by the tropics (Figure S1), accounting
6 for $> 90 \%$ during the northern hemisphere winter months (November – April) and 70% even
7 during the peak emissions from the northern boreal region during June and July (Sindelarova
8 et al., 2014). Despite annually averaged surface ozone mixing ratios being roughly a factor of
9 2 higher in the northern mid-high latitudes, monoterpene SCI production is still dominated by
10 the tropics. Annually averaged surface monoterpene SCI concentrations across the northern
11 boreal regions are $< 2 \times 10^3 \text{ cm}^{-3}$; during the summer months (JJA) this value rises to $2 - 5 \times$
12 10^3 cm^{-3} .

13 More than 97% of the total monoterpene derived SCI are SCI-B (Table 6). This is because
14 typical water vapour concentrations in the tropics are $> 5.0 \times 10^{17} \text{ cm}^{-3}$. This gives SCI-A
15 removal rates (i.e. $k_3[\text{H}_2\text{O}]$) of $2 \times 10^3 - 1.5 \times 10^5 \text{ s}^{-1}$, whereas removal rates of SCI-B to
16 unimolecular reactions have been determined here to be 1 – 3 orders of magnitude slower, on
17 the order of $100 - 250 \text{ s}^{-1}$. Since the loss of SCI-B is independent of temperature in the model,
18 the highest SCI-B concentrations would be expected to be located in the regions of highest
19 SCI-B production. Recent experimental studies (Smith et al., 2016) have demonstrated a
20 strong temperature dependence for the unimolecular decomposition rate of $(\text{CH}_3)_2\text{COO}$
21 between 283 and 323 K ($269 - 916 \text{ s}^{-1}$). Therefore, it may be that in reality there would be
22 some geographical variation in the rate of unimolecular loss.

23 The monoterpene SCI-A + H_2O reactions are expected to lead to high yields of both large
24 (e.g. Ma et al., 2008; Ma and Marston, 2008) and small (measured in high yield in the
25 experiments presented here) organic acids.

26 Figure 8 shows the seasonal removal of SO_2 by reaction with monoterpene derived SCI, as a
27 percentage of total gas-phase SO_2 oxidation in the surface layer. Monoterpene SCI are most
28 important (relative to OH) for SO_2 oxidation over tropical forests, where they account for up
29 to 50% of the local gas-phase SO_2 removal during DJF and MAM in some regions. The
30 reasons for this are two-fold: firstly, the highest modelled monoterpene SCI concentrations
31 are found in these regions (Figure 7); but additionally, OH concentrations in the model are
32 low over these areas (Figure S2). Historically there has been discrepancies between modelled



1 and observed OH concentrations over tropical forests, with models appearing to under-predict
2 [OH] by up to a factor of ten (e.g. Lelieveld et al., 2008). It was proposed that this was due to
3 missing sources of OH recycling during isoprene oxidation. During recent years there have
4 been advances in our understanding of isoprene chemistry. GEOS-Chem v-09, used here,
5 includes an isoprene OH recycling scheme largely based on Paulot et al. (2009a, 2009b), with
6 updates from Peeters et al. (2009), Peeters and Müller (2010), and Crouse et al. (2011;
7 2012), and evaluated in Mao et al. (2013). However, more recent experimental and theoretical
8 work is not yet included.

9 Annually, monoterpene SCI oxidation accounts for 1.1 % of the gas-phase SO₂ oxidation in
10 the terrestrial tropics. This accounts for the removal of 2.5 Gg of SO₂. Across the northern
11 boreal forests, monoterpene SCI contribute 0.5 % to gas-phase SO₂ removal annually,
12 removing 0.6 Gg of SO₂. Globally, throughout the whole atmosphere, monoterpene SCI
13 account for only 0.4 % of gas-phase SO₂ removal, removing 6.8 Gg of SO₂ annually.

14 It is noted that MEGAN does not contain oceanic monoterpene emissions, which may
15 increase the global importance of SCI for gas-phase SO₂ removal. Luo and Yu (2010)
16 determined annual global oceanic α -pinene emissions to be 29.5 TgC using a top-down
17 approach, with only 0.013 (Luo and Yu, 2010) – 0.26 (Hackenberg et al., 2017) TgC
18 estimated using a range of bottom-up approaches; clearly there are large uncertainties in
19 oceanic monoterpene emissions. At the upper end of this range they could potentially provide
20 a similar contribution to SCI production and subsequent SO₂ oxidation as monoterpenes
21 emitted from the terrestrial biosphere. SCI production more generally could be further
22 amplified by sources such as marine-derived alkyl iodine photolysis.

23 Blitz et al. (2017) recently calculated a revised SO₂ + OH reaction rate (k_I (1 bar N₂) (298 K)
24 = $5.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), based on experimental work and a master equation analysis, which is ~
25 40 % lower than the rate given in the most recent JPL data evaluation (Burkholder et al.,
26 2015) (k_I (1 bar N₂) (298 K) = $9.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), which is used in the GEOS-Chem model
27 simulation. Figure S3 shows the increased influence of monoterpene derived SCI on gas-
28 phase SO₂ oxidation if the alternative SO₂ + OH rate is used. This increased the impact of
29 monoterpene SCI to up to 60 % of gas-phase SO₂ removal in regions of the tropical forests
30 during DJF and MAM, with the contribution of monoterpene SCI to global gas-phase SO₂
31 oxidation increasing to 0.6 %.



1 While certain monoterpenes appear to be more important than others with regard to the
2 production of SCI which will oxidise SO₂, these results are sensitive to the kinetics used and
3 the assumptions made for the monoterpenes not studied experimentally here. Hence we do not
4 attempt to draw any conclusions about the relative importance of each monoterpene from the
5 modelling. Clearly the most important monoterpenes will be those with high yields of SCI-B,
6 particularly if those SCI-B have a structure that hinders unimolecular decomposition (such as
7 certain β-pinene derived SCI).

8

9 **7 Discussion and Atmospheric Implications**

10 Monoterpene ozonolysis produces a diverse range of SCIs, with contrasting fates in the
11 atmosphere, dominated by unimolecular reaction or reaction with water vapour, but which
12 may still affect atmospheric SO₂ processing. Monoterpene-derived SCI have the potential to
13 make a significant contribution to gas-phase SO₂ oxidation in specific local (i.e. forested)
14 environments, of up to 50 % at certain times of year - amplifying sulfate aerosol formation,
15 reducing the atmospheric lifetime and hence geographic distribution of SO₂, however the
16 results presented here show that their impact upon annual SO₂ oxidation globally is modest.
17 The results presented here demonstrate that it is important that monoterpene ozonolysis
18 reactions are considered to produce at least two different SCI species if their chemistry is to
19 be adequately represented in global models. This is because even a ‘moderate’ reaction rate
20 with water would be a dominant sink of an SCI with the averaged properties of SCI-A and
21 SCI-B.

22 SCI concentrations are expected to vary greatly depending on the local environment and time
23 of year, *e.g.* monoterpene abundance may be considerably higher (and with a different
24 reactive mix of alkenes giving a range of structurally diverse SCI) in a forested environment,
25 compared to a rural background. Furthermore, biogenic isoprene and monoterpene emissions
26 are strongly temperature dependent, hence are predicted to change significantly in the future
27 as a response to a changing climate and other environmental conditions (Peñuelas and Staudt,
28 2010).

29 This study shows that the ozonolysis of monoterpenes may contribute to significant SCI
30 concentrations in forested areas. Another group of compounds produced by forests that may
31 also have the potential to be a significant source of SCI are sesquiterpenes (C₁₅H₂₄). Although



1 generally present at low mixing ratios, this is due to their short atmospheric lifetimes caused
2 by their rapid reaction rates with ozone. The flux through the alkene-ozone reaction for fast
3 reacting monoterpenes and sesquiterpenes is often higher than for monoterpenes with high
4 mixing ratios but low removal rates, e.g. α -pinene and β -pinene. Ozonolysis of sesquiterpenes
5 has been shown to have very high SCI yields (Beck et al., 2011; Yao et al., 2014) and these
6 SCI have been shown to react with SCI scavengers (e.g. SO_2 , H_2O etc.) in a similar way to
7 smaller SCI (Yao et al., 2014). It has been predicted that SCI from sesquiterpenes may have a
8 high degree of secondary ozonide formation (Chuong et al., 2004) but experimental work has
9 shown very different results for structurally different sesquiterpenes studied (Beck et al.,
10 2011; Yao et al., 2014) hence this is highly uncertain, as is the fate of the SOZ once formed.
11 Therefore, these have the potential to be another significant source of SCI.

12

13 **8 Conclusions**

14 We report results from an integrated experimental (simulation chamber), theoretical (quantum
15 chemical) and modelling (global chemistry-transport simulation) study of the impacts of
16 monoterpene ozonolysis reactions on stabilised Criegee intermediate (SCI) formation and SO_2
17 oxidation. The ozonolysis of the monoterpenes α -pinene, β -pinene and limonene have been
18 shown to produce a structurally diverse range of chemically distinct SCIs, with some showing
19 limited sensitivity to / reaction with water vapour under near-atmospheric humidity levels. A
20 multi-component system is required to explain the experimentally observed SO_2 removal
21 kinetics. A two-body model system based on the assumption of a fraction of the SCI produced
22 being reactive towards water (SCI-A; potentially contributing to the significant formation of a
23 range of organic acids in the atmosphere), and a fraction being relatively unreactive towards
24 water (SCI-B), analogous to the structural dependencies observed for the simpler CH_3CHOO
25 SCI system, has been shown to describe the observed kinetic data reasonably well for all the
26 monoterpene systems investigated, and may form a computationally affordable and
27 conceptually accessible basis for the description of this chemistry within atmospheric models.
28 The atmospheric fate of SCI-B produced from the monoterpenes studied here will be
29 controlled by their removal by unimolecular decomposition. In this work, we have
30 experimentally determined the monoterpene SCI-B decomposition rate to be between 100 and
31 250 s^{-1} . This has significant implications for the role of monoterpene derived SCI as oxidants
32 in the atmosphere. The fate of SCI-A will be reaction with water or the water dimer, likely
33 leading to the production of a range of organic acids.



1 A theory-based analysis of the kinetics of the SCI formed from α -pinene, β -pinene ozonolysis
2 has also been performed, which complements the experimental work. The identification of the
3 likely SCI-A and SCI-B populations and the derived kinetics agree with experimental
4 observations within the respective uncertainties.

5 A modelling study using the GEOS-Chem global 3-D chemical transport model supplemented
6 with the chemical kinetics elucidated in this work suggests that the global monoterpene
7 derived SCI burden will be dominated ($> 97\%$) by SCI-B. The highest annually averaged SCI
8 concentrations are found in the tropics, with seasonally averaged monoterpene SCI
9 concentrations up to $1.2 \times 10^4 \text{ cm}^{-3}$ owing to large monoterpene emissions. Across the boreal
10 forest, average SCI concentrations reach between $3 - 5 \times 10^3 \text{ cm}^{-3}$ during the northern
11 hemisphere summer. Oxidation of SO_2 by monoterpene SCI is shown to also be most
12 important in the tropics. While oxidation by SCI contributes $< 1\%$ to gas-phase SO_2 oxidation
13 globally, over tropical forests this can rise to up to 50 % at certain times of the year.
14 Monoterpene SCI driven SO_2 oxidation will increase the production of sulfate aerosol –
15 affecting atmospheric radiation transfer, and hence climate; and reduce the atmospheric
16 lifetime and hence transport of SO_2 . These effects will be substantial in areas where
17 monoterpene emissions are significant, in particular over the Amazon, Central Africa and SE
18 Asian rainforests.

19

20

21 **Data Availability**

22 Experimental data will be made available in the Eurochamp database (www.eurochamp.org)
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24

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1 Table 1. Monoterpene SCI yields derived in this work and reported in the literature.

ϕ_{SCI}	Reference	Notes	Methodology
<i>α-pinene</i>			
0.19 (\pm 0.01)	This work		SO ₂ loss
0.15 (\pm 0.07)	Sipilä et al. (2014)		Formation of H ₂ SO ₄
0.22	Taipale et al. (2014) (personal comm. Berndt)		
0.125 (\pm 0.04)	Hatakeyama et al. (1984)		Formation of H ₂ SO ₄
0.20	MCMv3.3.1 ^a		
<i>β-pinene</i>			
0.60 (\pm 0.03)	This work		SO ₂ loss
0.46	Ahrens et al. (2014)	$\phi_{\text{C9-SCI}}$: 0.36 ϕ_{CH2OO} : 0.10	FTIR detection
0.25	MCMv3.3.1 ^a	$\phi_{\text{C9-SCI}}$: 0.102 ϕ_{CH2OO} : 0.148	
0.42	Nguyen et al. (2009)	$\phi_{\text{C9-SCI}}$: 0.37 ϕ_{CH2OO} : 0.05	Theoretical
0.51	Winterhalter et al. (2000)	$\phi_{\text{C9-SCI}}$: 0.35 ϕ_{CH2OO} : 0.16	Change in nopinone yields $f([\text{H}_2\text{O}])$
0.44	Kotzias et al. (1990)		Formation of H ₂ SO ₄
0.25	Hatakeyama et al. (1984)		Formation of H ₂ SO ₄
0.30	Zhang and Zhang (2005)	$\phi_{\text{C9-SCI}}$: 0.22 ϕ_{CH2OO} : 0.08	
> 0.27	Ma and Marston (2008)	$\phi_{\text{C9-SCI}}$: 0.27 ϕ_{CH2OO} : 0.16 ^a ϕ_{CH2OO} : 0.06 ^b	Change in nopinone yields $f([\text{H}_2\text{O}])$
0.27	Hasson et al. (2001)		Change in nopinone yields $f([\text{H}_2\text{O}])$
<i>Limonene</i>			
0.23 (\pm 0.01)	This work		SO ₂ loss
0.27 (\pm 0.12)	Sipilä et al. (2014)		Formation of H ₂ SO ₄
0.34	Leungsakul et al. (2005)	$\phi_{\text{C10-SCI}}$: 0.26 $\phi_{\text{Cl-x}}$: 0.04 ϕ_{CH2OO} : 0.05	Measurement of stable particle and gas-phase products
0.135	MCMv3.3.1 ^a		



- 1 Uncertainty ranges ($\pm 2\sigma$, parentheses) indicate combined precision and systematic measurement error
- 2 components for this work, and are given as stated for literature studies. All referenced experimental studies
- 3 produced SCI from MT + O₃ and were conducted between 700 and 760 Torr. ^a <http://mcm.leeds.ac.uk/MCM/>
- 4 (Jenkin et al., 2015).
- 5 ^a assuming 100 % stabilisation
- 6 ^b assuming 40 % stabilisation


 1 Table 2. Monoterpene derived SCI relative and absolute^a rate constants derived in this work.

SCI	$10^5 k_3/k_2$	$10^{15} k_3$ ($\text{cm}^3 \text{s}^{-1}$)	$10^{-12} k_d/k_2$ (cm^{-3})	k_d (s^{-1})
<i>α-pinene</i>				
SCI-A	> 140 (± 34)	> 310 (± 75) ^a		
SCI-B			< 8.2 (± 1.5)	< 240 (± 44) ^c
<i>β-pinene</i>				
SCI-A	> 10 (± 2.7)	> 4 (± 1) ^b		
SCI-B			< 6.0 (± 1.3)	< 170 (± 38) ^c
<i>Limonene</i>				
SCI-A	< 3.5 (± 0.2)	< 7.7 (± 0.6) ^a		
SCI-B			> 4.5 (± 0.1)	> 130 (± 3) ^c

2 Uncertainty ranges ($\pm 2\sigma$, parentheses) indicate combined precision and systematic measurement error
 3 components. ^a Scaled to an absolute value using $k_2(\text{anti-CH}_3\text{CHOO}) = 2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Sheps et al., 2014); ^b
 4 Scaled to an absolute value using $k_2(\text{anti-CH}_3\text{CHOO}) = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Ahrens et al., 2014); ^c Scaled using
 5 $k_2(\text{syn-CH}_3\text{CHOO}) = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Sheps et al., 2014).

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- 1 Table 3. Unimolecular reactions for the CI derived from α -pinene, β -pinene, and *d*-limonene,
 2 as derived by Vereecken et al. (2017). Barrier heights (kcal mol⁻¹) listed estimate post-
 3 CCSD(T) energies.

Carbonyl oxide	Reaction	E_b	$k(298\text{K}) / \text{s}^{-1}$
<i>α-pinene</i>			
CI-1a	1,4-H-migration	15.8	600
	SOZ-formation	15.6	5×10^{-2}
	1,3-ring closure	21.6	1×10^{-3}
CI-1b	1,3-ring closure	14.8	60
	1,3-H-migration	29.0	1×10^{-6}
CI-2a	1,4-H-migration	16.3	250
	1,3-ring closure	20.8	6×10^{-3}
CI-2b	1,4-H-migration	17.0	60
	SOZ-formation	13.5	8
	Ring closure	19.9	3×10^{-2}
<i>β-pinene</i>			
CI-3	1,4-H-migration	15.7	375
	1,3-ring closure	21.1	2×10^{-3}
CI-4	1,3-ring closure	17.2	2.0
	Ring opening	23.6	(Slow, Nguyen et al. 2009a)
	1,4-H-migration	24.9	(Slow, Nguyen et al. 2009a)
CH ₂ OO	1,3-ring closure	19.0	0.3
	1,3-H-migration	30.7	1×10^{-7}
<i>Limonene^a</i>			
CI-5a	1,4-H-migration	SAR	200 ^a
CI-5b	1,3-ring closure	SAR	75 ^a
CI-6a	1,4-H-migration	SAR	430 ^a
CI-6b	1,4-H-migration	SAR	700 ^a
CI-7a	1,4-H-migration	SAR	15
CI-7b	1,4-H-migration	SAR	600

- 4 ^a Formation of secondary ozonides (SOZ) is not included, and could be the dominant unimolecular loss.

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1 Table 4. Rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction of CI with H_2O and $(\text{H}_2\text{O})_2$ as
 2 predicted by Vereecken et al. (2017). Values are based on explicit CCSD(T)/aug-cc-
 3 pVTZ//M06-2X/aug-cc-pVTZ calculations and multi-conformer TST, including empirical
 4 corrections to reference experimental data, except for limonene-derived CI where the values
 5 are predicted using a structure-activity relationship. The rate coefficients for CH_2OO ,
 6 CH_3CHOO , and $(\text{CH}_3)_2\text{COO}$ are within a factor of 4 of evaluated literature data (Vereecken et
 7 al., 2017).

Carbonyl oxide	$k(298\text{K}) \text{H}_2\text{O}$	$k(298\text{K}) (\text{H}_2\text{O})_2$
CH_2OO	8.7×10^{-16}	1.4×10^{-12}
<i>syn</i> - CH_3CHOO	6.7×10^{-19}	2.1×10^{-15}
<i>anti</i> - CH_3CHOO	2.3×10^{-14}	2.7×10^{-11}
$(\text{CH}_3)_2\text{COO}$	7.5×10^{-18}	1.8×10^{-14}
<i>α-pinene</i>		
CI-1a	1.3×10^{-18}	2.9×10^{-15}
CI-1b	1.5×10^{-14}	1.7×10^{-11}
CI-2a	1.0×10^{-18}	2.5×10^{-15}
CI-2b	2.4×10^{-19}	7.0×10^{-16}
<i>β-pinene</i>		
CI-3	1.7×10^{-18}	4.3×10^{-15}
CI-4	4.2×10^{-16}	6.4×10^{-13}
<i>Limonene</i>		
CI-5a	1.5×10^{-18}	4.3×10^{-15}
CI-5b	1.5×10^{-14}	1.7×10^{-11}
CI-6a	9.1×10^{-18}	2.1×10^{-14}
CI-6b	1.5×10^{-17}	3.2×10^{-14}
CI-7a	9.7×10^{-18}	1.9×10^{-14}
CI-7b	4.3×10^{-18}	1.1×10^{-14}

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1 Table 5. Kinetic parameters used in the global modelling study.

SCI	ϕ_{SCI}	$10^{15} k_3$ ($\text{cm}^3 \text{s}^{-1}$)	$10^{11} k_2^a$ ($\text{cm}^3 \text{s}^{-1}$)	k_d (s^{-1})
<i>α-pinene</i>				
SCI-A	0.08	310	22	-
SCI-B	0.11	-	2.9	240
<i>β-pinene</i>				
SCI-A	0.25	4	4	-
SCI-B	0.35	-	2.9	170
<i>Limonene</i>				
SCI-A	0.05	7.7	22	-
SCI-B	0.18	-	2.9	130
<i>Myrcene</i>				
SCI-B	0.30	-	13 ^b	819 ^c
<i>Ocimene</i>				
SCI-B	0.30	-	13 ^b	819 ^c
<i>Sabinene</i>^d				
SCI-A	0.25	4	4	-
SCI-B	0.35	-	2.9	170
<i>3-carene</i>^e				
SCI-A	0.08	310	22	-
SCI-B	0.11	-	2.9	240

2 ^a $k_2(\text{SCI-A}+\text{SO}_2)$ from ($\text{SO}_2+\textit{anti}$ - CH_3CHOO) - Sheps et al. (2014); $k_2(\text{SCI-B}+\text{SO}_2)$ from ($\text{SO}_2+\textit{syn}$ - CH_3CHOO)

3 - Sheps et al. (2014) unless otherwise stated

4 ^b $k_2(\text{SCI-B}+\text{SO}_2)$ from ($\text{SO}_2+\textit{anti}$ - $(\text{CH}_3)_2\text{COO}$) – Huang et al. (2015)5 ^c $k_d(\text{SCI-B})$ from Newland et al. (2015) (scaled to $k_2(\text{SCI-B}+\text{SO}_2)$ from Huang et al. (2015))6 ^d Kinetics based on β -pinene7 ^e Kinetics based on α -pinene

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1 Table 6. Monoterpene contribution to [SCI] and SO₂ oxidation in the surface layer of the
2 model simulation.

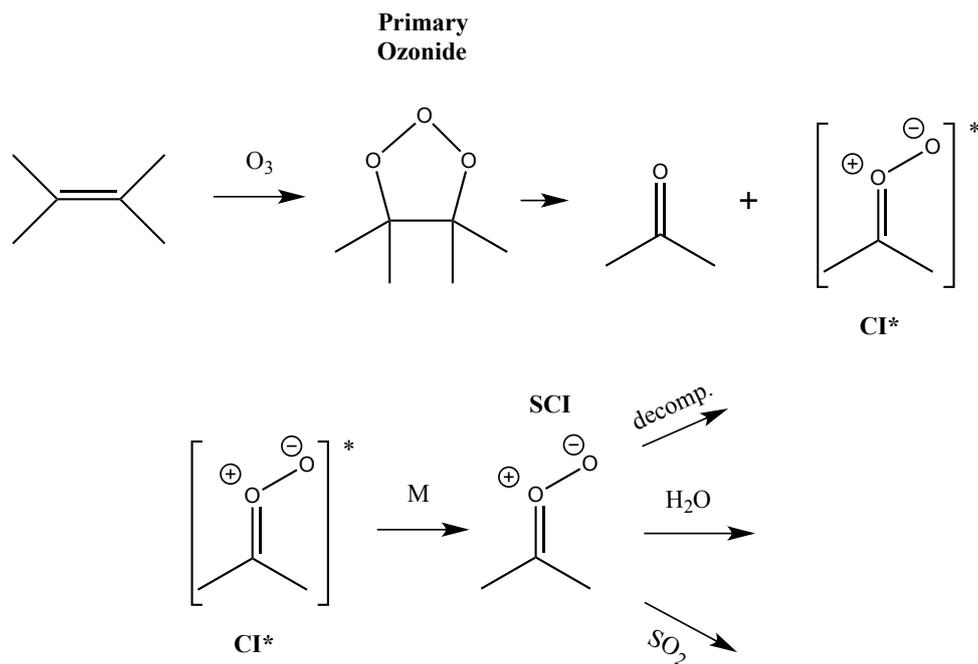
Monoterpene	Annual emissions ^a (Tg C)	% contribution to [SCI-A]	% contribution to [SCI-B]	% contribution to SO ₂ oxidation
α -pinene	35.4	0.5	16	6.9
β -pinene	16.9	74	46	65
limonene	9.2	3.5	14	7.2
myrcene	3.1	0.0	1.2	4.5
trans- β -ocimene	14.1	0.0	5.4	11
sabinene	7.9	22	14	4.5
3-carene	6.4	0.0	2.7	1.6

3 ^a From MEGAN v2.1 (Guenther et al., 2012)

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3 Scheme 1. Simplified generic mechanism for the reaction of Criegee Intermediates (CIs)

4 formed from alkene ozonolysis.

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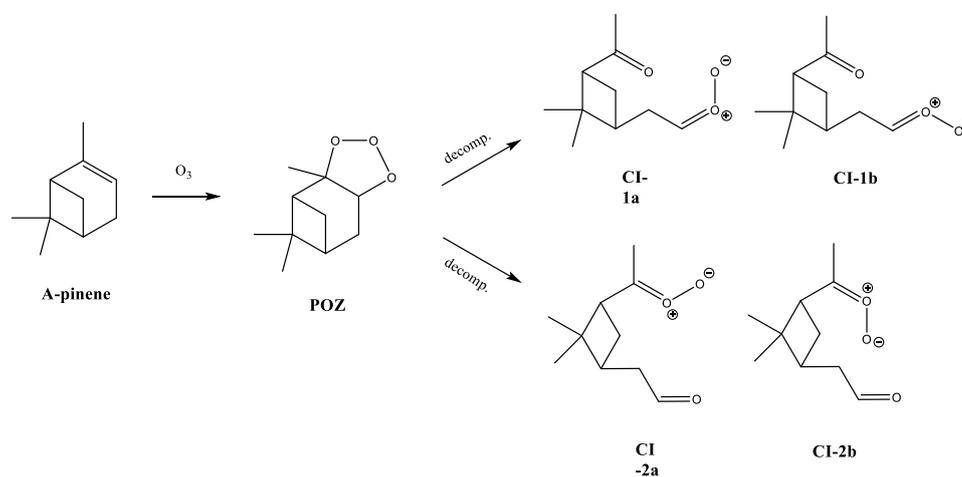
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3 Scheme 2. Mechanism of formation of the two Criegee Intermediates (CIs) from α -pinene
4 ozonolysis.

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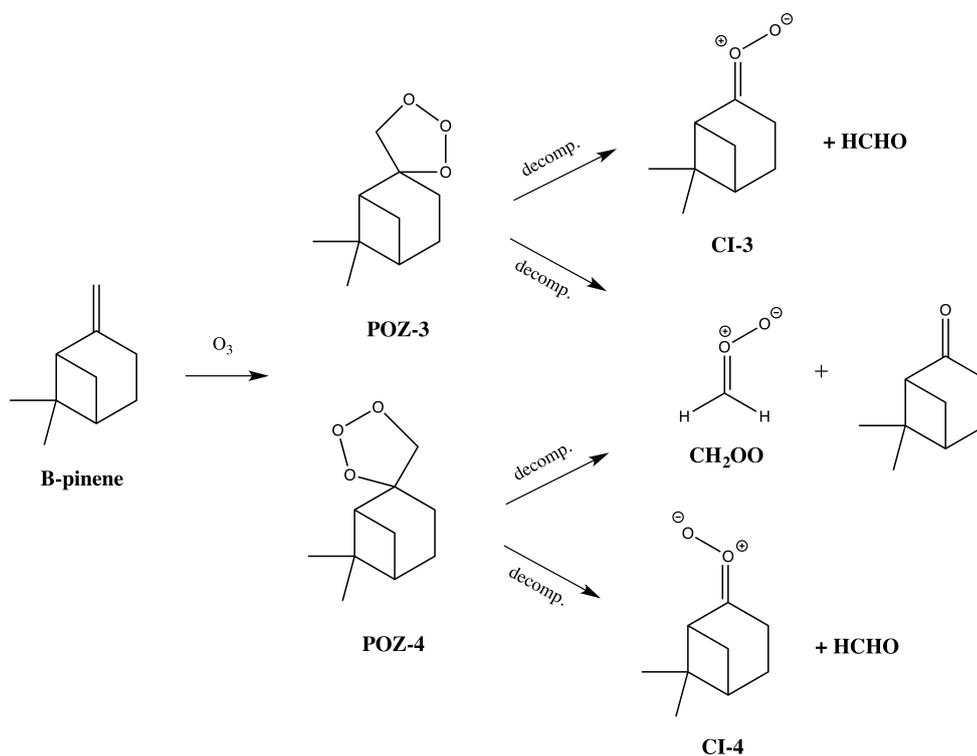
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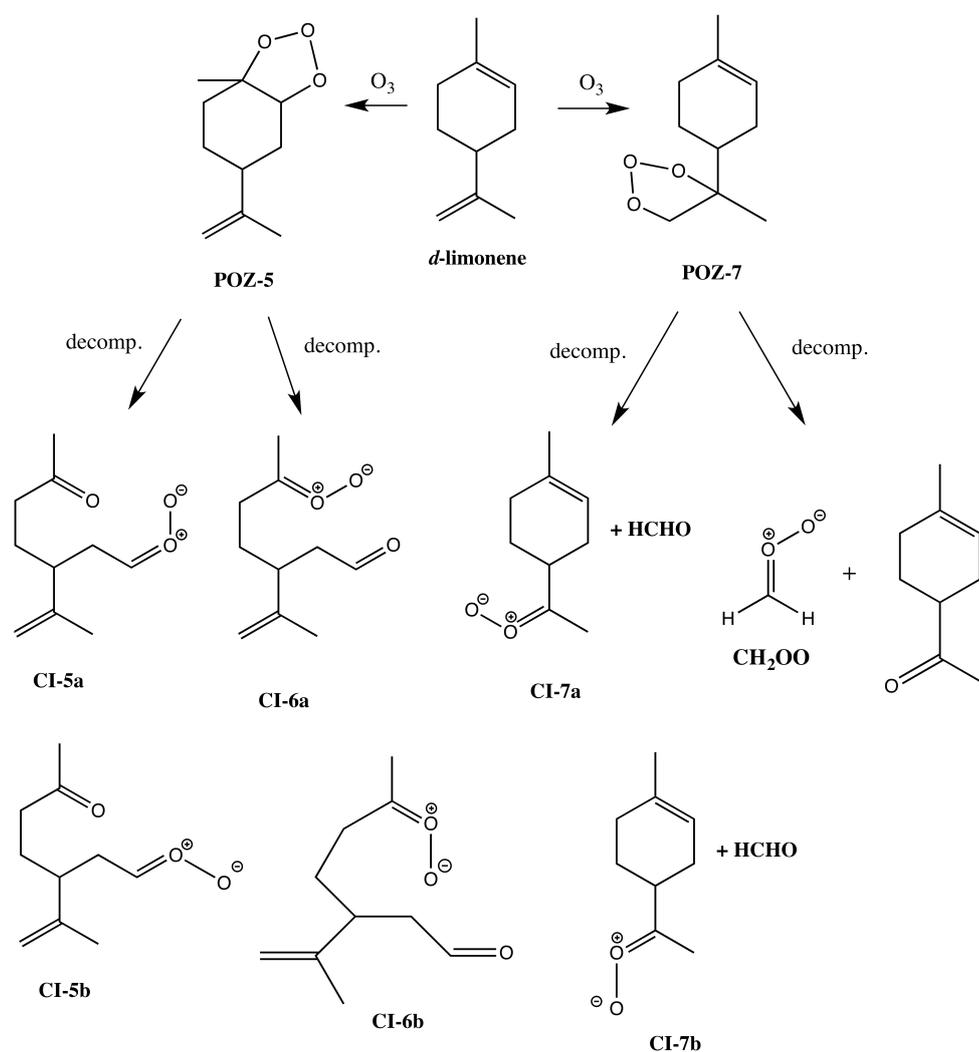


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3 Scheme 3. Mechanism of formation of the three Criegee Intermediates (CIs) from β -pinene

4 ozonolysis.



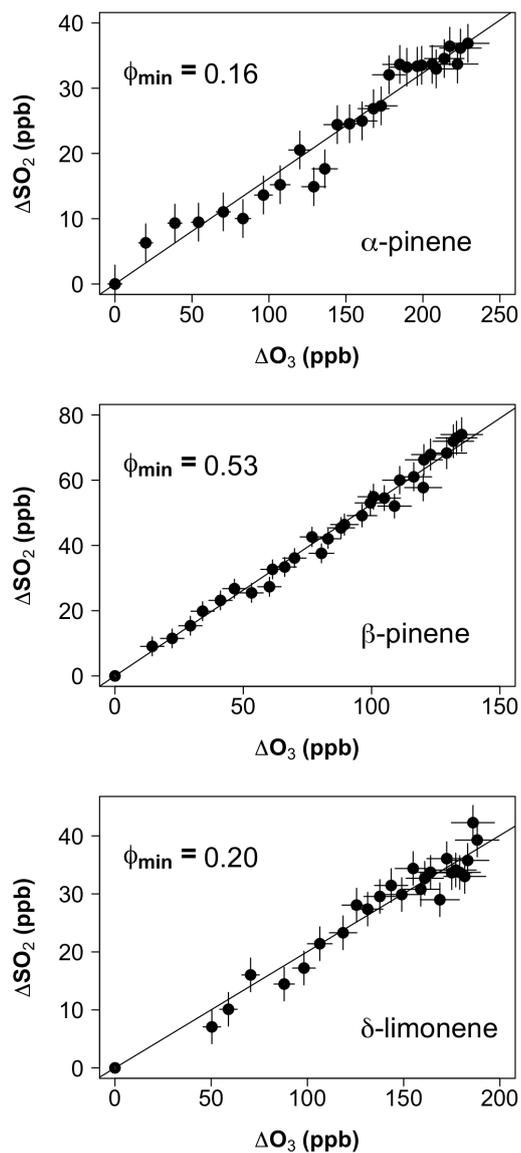
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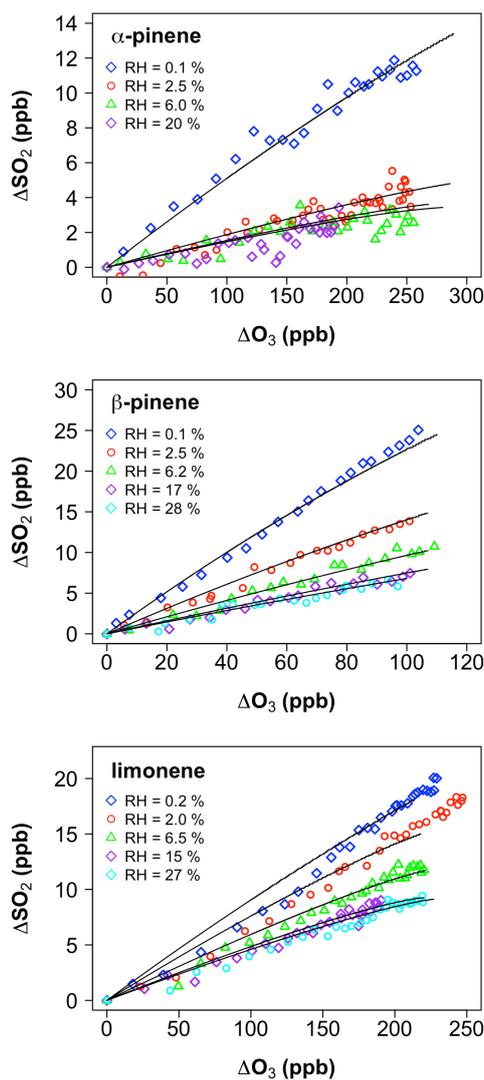
3 Scheme 4. Mechanism of formation of the four Criegee Intermediates (CIs) from limonene

4 ozonolysis.

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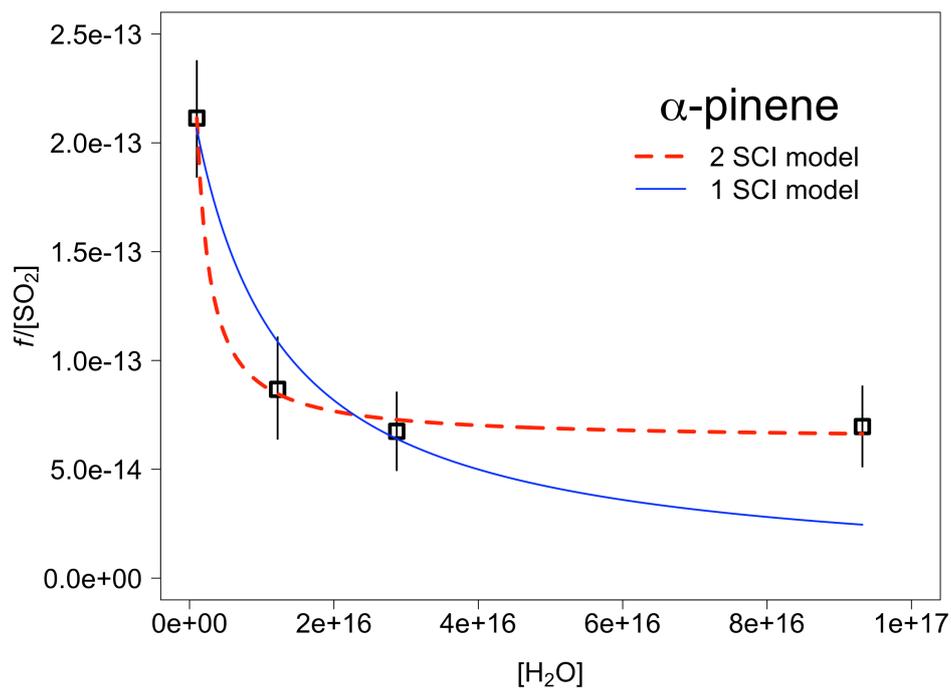


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2 Figure 1. ΔSO_2 vs. ΔO_3 during excess SO_2 experiments ($[\text{H}_2\text{O}] < 5 \times 10^{15} \text{ cm}^{-3}$). The gradient
3 determines the minimum SCI yield (ϕ_{\min}).
4



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2 Figure 2. Cumulative consumption of SO_2 as a function of cumulative consumption of O_3 ,
3 ΔSO_2 versus ΔO_3 , for the ozonolysis of α -pinene, β -pinene and limonene in the presence of
4 SO_2 at a range of water vapour concentrations, from $1 \times 10^{15} \text{ cm}^{-3}$ to $1.9 \times 10^{17} \text{ cm}^{-3}$. Symbols
5 are experimental data, corrected for chamber dilution. Lines are smoothed fits to the
6 experimental data.

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2 Figure 3. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation
3 E1) to the measured values (open squares) of $f/[\text{SO}_2]$ for α -pinene. From the fit we derive
4 relative rate constants for reaction of the α -pinene derived SCI, SCI-A and SCI-B with H₂O
5 (k_3/k_2) and decomposition ($(k_d+L)/k_2$) assuming that $\gamma^A = 0.40$ and $\gamma^B = 0.60$.

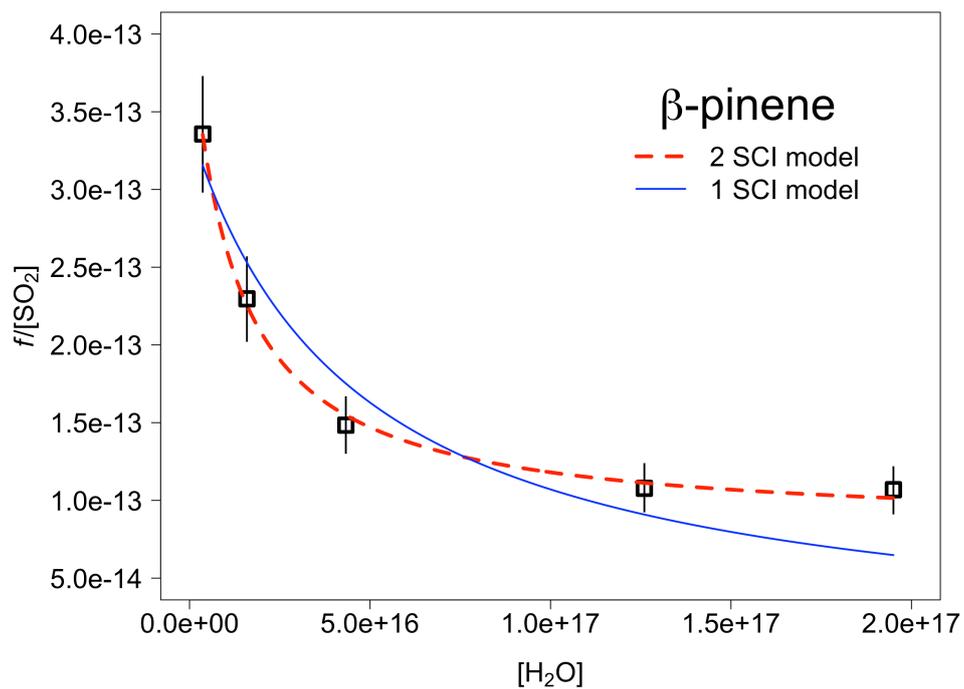
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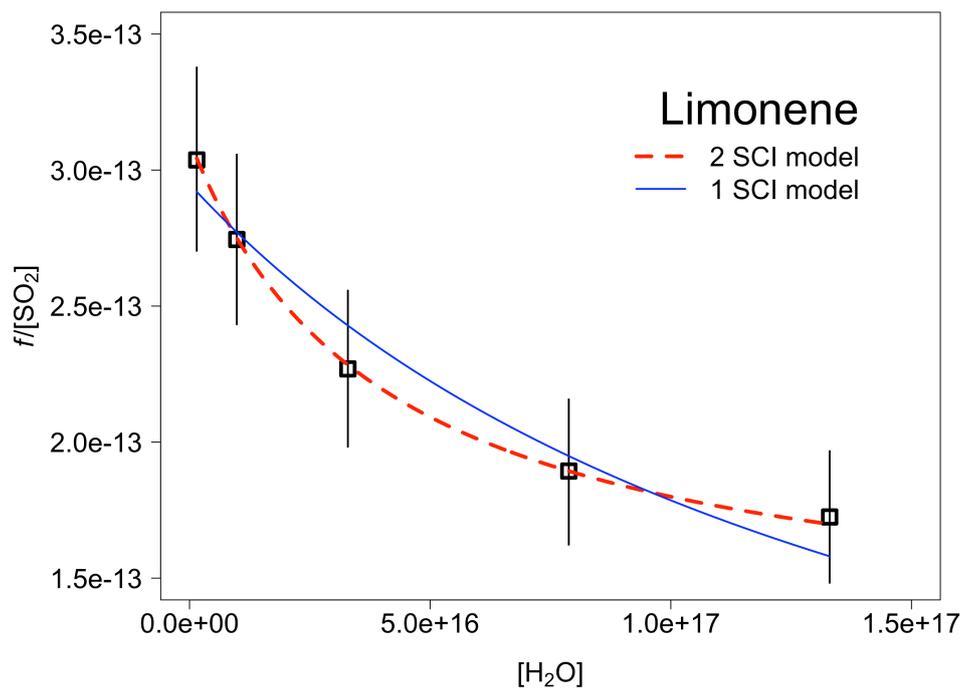
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2 Figure 4. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation
3 E1) to the measured values (open squares) of $f/[\text{SO}_2]$ for β -pinene. From the fit we derive
4 relative rate constants for reaction of the β -pinene derived SCI, SCI-A and SCI-B with H_2O
5 (k_3/k_2) and decomposition ($(k_d+L)/k_2$) assuming that $\gamma^A = 0.41$ and $\gamma^B = 0.59$.



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3 Figure 5. Application of a 2 SCI model fit (Equation E4) and a single SCI model fit (Equation

4 E1) to the measured values (open squares) of $f/[\text{SO}_2]$ for limonene. From the fit we derive5 relative rate constants for reaction of the limonene derived SCI, SCI-A and SCI-B with H₂O6 (k_3/k_2) and decomposition ($(k_d+L)/k_2$) assuming that $\gamma^A = 0.22$ and $\gamma^B = 0.78$.

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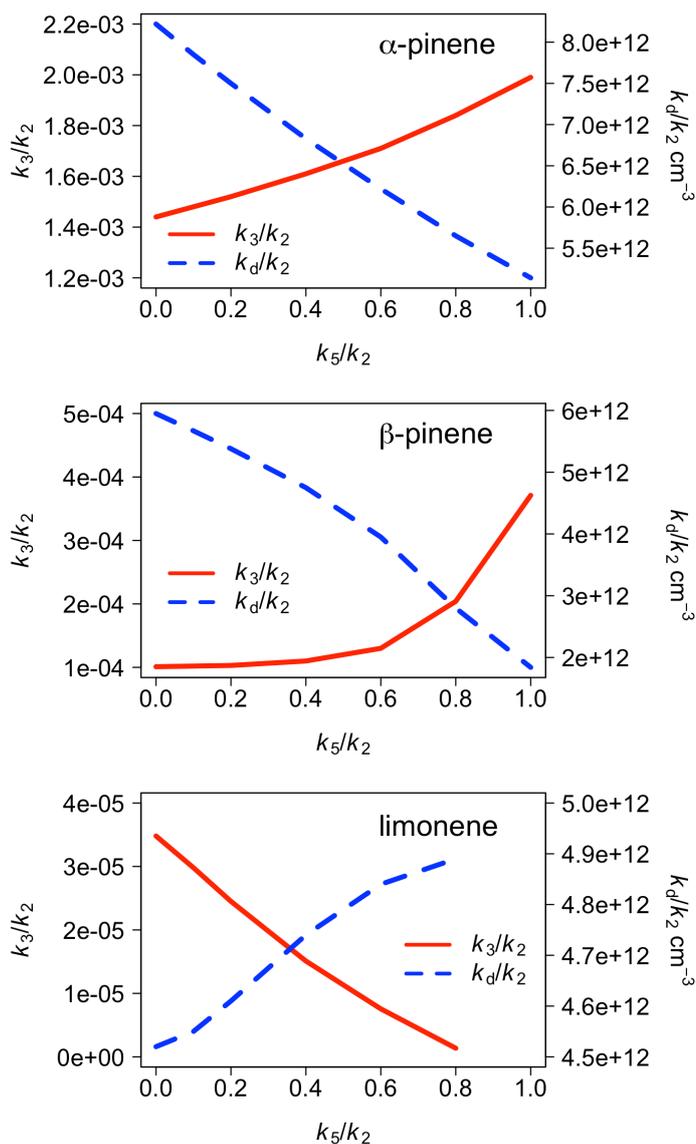
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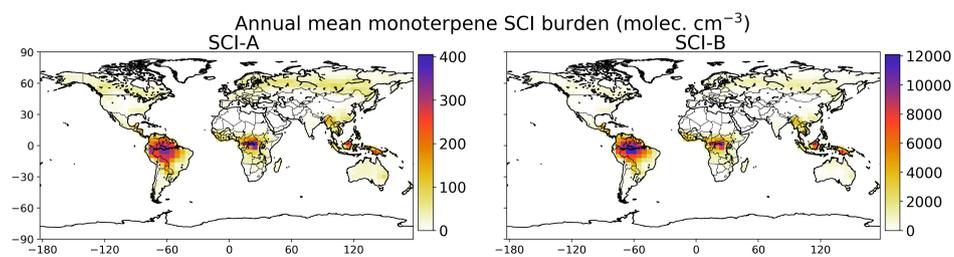
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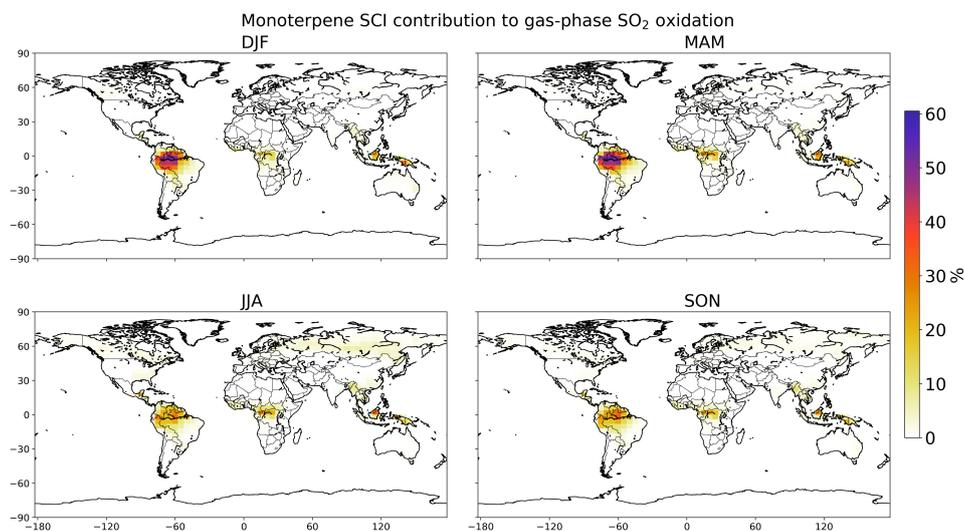
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 2 Figure 6. Variation of k_3/k_2 ($k(\text{SCI-A}+\text{H}_2\text{O})/(k(\text{SCI-A}+\text{SO}_2))$) and k_d ($k(\text{SCI-B}$
 3 $\text{unimol.})/(k(\text{SCI-B}+\text{SO}_2))$) as a function of the ratio k_5/k_2 ($k(\text{SCI}+\text{acid})/k(\text{SCI}+\text{SO}_2)$), derived
 4 from least squares fit of Equation E4 to measurements shown in Figures 3 -5 for α -pinene, β -
 5 pinene and limonene respectively.

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Figure 7. Annual mean monoterpene SCI-A and SCI-B concentrations (cm^{-3}) in the surface layer of the GEOS-Chem simulation.



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2 Figure 8. Seasonal SO₂ oxidation by monoterpene SCI as percentage of total gas-phase SO₂
3 oxidation in the surface layer.

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