1 **Computational investigation into the gas-phase ozonolysis** 2 **of the conjugated monoterpene α -phellandrene[†]**

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6 [†]Electronic supplementary information available: additional discussion, tables,
7 figures and reactions equations and quantum chemical data for all species
8 discussed in this paper.

9

10 **Abstract**

11 Reaction with ozone is a major atmospheric sink for α -phellandrene, a
12 monoterpene found in both the indoor and outdoor environments, however
13 experimental literature concerning the reaction is scarce. In this study, high-level
14 G4(MP2) quantum chemical calculations are used to theoretically characterise
15 the reaction of ozone with both double bonds in α -phellandrene for the first
16 time. Results show that addition of ozone to the least substituted double bond in
17 the conjugated system is preferred. Following addition, thermal and chemically
18 activated unimolecular reactions, including the so-called hydroperoxide and
19 ester or 'hot' acid channels, and internal cyclisation reactions, are characterised
20 to major first generation products. Conjugation present in α -phellandrene allows
21 two favourable Criegee intermediate reaction pathways to proceed that have not
22 previously been considered in the literature; namely a 1,6-allyl resonance
23 stabilised hydrogen shift and intramolecular dioxirane isomerisation to an
24 epoxide. These channels are expected to play an important role alongside

conventional routes in the ozonolysis of α -phellandrene. Computational characterisation of the potential energy surface thus provides insight into this previously unstudied system, and will aid future mechanism development and experimental interpretation involving α -phellandrene and structurally similar species, to which the results are expected to extend.

1. Introduction

Biogenic sources dominate the global emission budget of volatile organic compounds into the atmosphere, with monoterpenes accounting for a significant fraction of nonmethane hydrocarbons emitted.¹⁻⁴ Considering source strength, estimated to be 30 – 127 Tg C year⁻¹, along with high chemical reactivity,^{5,6} monoterpenes are thought to play an important role in the chemistry of the atmosphere; influencing its oxidative capacity, the tropospheric ozone budget and by producing secondary organic aerosol (SOA) which impacts both health and climate.⁷⁻¹¹ Indeed the ozonolysis of monoterpenes is thought to be one of the major sources of SOA in the atmosphere.¹²

Despite extensive experimental work on the ozonolysis of monoterpenes,^{5,6,10,13-18} there is still considerable uncertainty in their reaction mechanisms. The Criegee mechanism, that is, concerted cycloaddition of ozone to the double bond of the alkene forming a 1,2,3-trioxolane intermediate species (primary ozononide, POZ), is widely accepted,^{5,19} however experimental detection of intermediate species is extremely difficult due to their short lifetimes. Attempts at coupling experimental results with proposed mechanisms are often hindered by uncertainty in the fates of reactive intermediates. In addition, competition

between prompt unimolecular and bimolecular reactions may result in pressure- and time-dependent yields. Inevitably theoretical studies have been utilised to describe the intricacies involved in the monoterpene ozonolysis.²⁰⁻²⁶

One monoterpene that has received some attention in the literature is α -phellandrene. Emitted by a variety of plants²⁷⁻³² and found in the indoor setting as an additive to household cleaning products and air fresheners,^{33,34} α -phellandrene is an extremely reactive monoterpene with a large SOA forming potential,³⁵ that can have an immediate impact on the environment to which it is emitted. The rate constant of α -phellandrene with ozone has been measured in a number of studies,³⁶⁻³⁸ with a rate constant of $3.0 \times 10^{-15} (\pm 35\%) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ favoured.⁵ Less information is available on the products of the reaction; with OH radical yields of 26 – 31% and 8 – 11% reported for the ozonolysis of the two double bonds³⁹ and acetone having been measured as a minor product (< 2%).⁴⁰

Whilst experimental data is sparse, α -phellandrene is an interesting species for theoretical appraisal, containing a cyclic, conjugated moiety that has not previously been investigated in the literature. In this study the reaction mechanism of ozone with α -phellandrene is elucidated, including formation of POZs, subsequent cleavage to form Criegee intermediates (CIs), and unimolecular reactions of the CIs to first generation products. A generalised scheme is shown in Figure 1. Density functional theory (DFT) and *ab initio* methods are employed to obtain accurate geometries and energies of transition states (TSs), reactive intermediates, and products, thus producing a potential energy surface (PES) that identifies key reaction pathways. Results show

unconventional routes, which have not previously been considered in the ozonolysis of alkenes, are important in the decomposition of the conjugated system. These findings potentially extend to other structurally similar compounds. Key species that are likely to be important first generation products in the ozonolysis of α -phellandrene are also described.

2. Computational Methods

The high-level composite G4(MP2) theory was used in order to explore the Gibbs-free energy surface at 298 K for the reaction of ozone with α -phellandrene.⁴¹ The G4(MP2) composite protocol is an efficient composite procedure for approximating the CCSD(T) (coupled cluster energy with singles, doubles, and quasiperturbative triple excitations) energy in conjunction with a large triple- ζ -quality basis set.^{42,43} This protocol is widely used for the calculation of thermochemical and kinetic properties (for a recent review of the G_n methods see Curtiss *et al.*⁴²). G4(MP2) theory has been found to produce thermochemical gas-phase properties (such as reaction energies, bond dissociation energies, and enthalpies of formation) with a mean absolute deviation of 4.4 kJ mol⁻¹ from the 454 experimental energies of the G3/05 test set.^{41,44} It has also been found that G4(MP2) shows a similarly good performance for reaction barrier heights.⁴⁵⁻⁴⁸ The geometries of all structures have been optimized at the B3LYP/6-31G(2df,p) level of theory as prescribed in the G4(MP2) procedure.^{41,49-51} Harmonic vibrational analyses have been performed to confirm each stationary point as either an equilibrium structure (i.e., all real frequencies) or a transition structure (i.e., with one imaginary frequency). Zero-point vibrational energy (ZPVE), thermal enthalpy ($H_{298}-H_0$), and entropy (S) corrections were obtained from

these frequencies within the rigid rotor-harmonic oscillator approximation and are used for converting the G4(MP2) electronic energies into Gibbs free energies at 298K (ΔG_{298}). The connectivities of the local minima and saddle points were confirmed by performing intrinsic reaction coordinate (IRC) calculations.^{52,53} These calculations were carried out at the B3LYP/6-31+G(d) level of theory. All calculations were carried out using the Gaussian 09 program suite.⁵⁴

3. Results and discussion

3.1 Formation of the CIs

The initial approach of ozone to the two double bonds of α -phellandrene can occur, in principle, on either side of the ring structure to produce four distinct POZ species. Additionally, each POZ formed has two conformers, depending on the relative spatial orientation of the central oxygen atom in the newly formed five-membered ring. Consequently, eight distinct reaction channels exist for the addition of ozone to α -phellandrene. The energy of the TS and POZ for each of these pathways is given in Table 1; with the more favourable attack site found to be dependent on the face of α -phellandrene that ozone approaches.

Frontier molecular orbital theory predicts that addition of ozone to the more substituted double bond (**C2** – **C3**, **DB1**) is favoured over addition to the less substituted double bond (**C6** – **C7**, **DB2**).¹⁹ Meanwhile experimental evidence from the ozonolysis of isoprene^{55–58} and miscellaneous conjugated dienes⁵⁹ shows addition to the less substituted double bonds is favoured, suggesting that steric effects are more influential. The driving steric factor in α -phellandrene is found to be the relative orientation of carbons **C4** and **C5**, which are buckled due

to ring strain and forced onto opposing sides of the plane formed by the conjugated carbons. The relative orientation of **C4/C5** is thought to predominantly impact approach of ozone to the double bond to which it is adjacent, that is, if ozone approaches from the face where **C4** is notionally 'up', then **DB2** is favoured and vice versa, as seen in Figure 2. The effect is non-negligible, with differences greater than 4.4 kJ mol⁻¹ observed for analogous attacks from either face. We note that, according to the Arrhenius equation, a change of 5.7 kJ mol⁻¹ in the barrier corresponds to a change of one order of magnitude in the reaction rate at 298 K. Overall, addition to **DB2** has the lowest barriers, suggesting that addition to the least substituted double bond is favoured in α -phellandrene, consistent with what has been observed experimentally in other diene systems.⁵⁵⁻⁵⁹

Once the POZ ruptures, conformational isomerism resulting from differing attack faces disappears. For this reason, and to reduce computational costs, only four unique addition pathways are thought necessary for further analysis to capture the chemistry of α -phellandrene's ozonolysis; that being attack at either double bond with the central oxygen of the POZ both *syn* (**b**) and *anti* (**a**) to α -phellandrene's 6-membered carbon ring. Chirality effects were found to have no impact on results (S.1, ESI).

The PES for ozone addition to α -phellandrene is given in Figures 3 and 4. The reaction proceeds via formation of a van der Waals complex (**vdW1**, **vdW2**, **vdW3**, **vdW4**), followed by concerted cycloaddition through **TS1**, **TS2**, **TS3** and **TS4** to yield **POZ1a**, **POZ1b**, **POZ2a** and **POZ2b** respectively. The van der Waals

complexes and TSs both lie lower in electronic energy and enthalpy than the free reactants (S.2, ESI), such that addition of ozone to α -phellandrene is essentially a barrierless reaction. Formation of the van der Waals complex is accompanied by negligible structural perturbations compared to the reactants. Similarly, minor distortions of the reactants occur upon formation of the TS (bond changes less than 0.04 Å, ozone angle deviations less than 5°), with the majority of structural perturbations occurring after passing through the TS (e.g. S.3, ESI). Most notably, the C–O distances shrink whilst the C–C distance elongates to become a single bond. The calculated C–C and C–O bond distances for all POZs investigated ranged from 1.558 – 1.563 Å and 1.420 – 1.454 Å respectively, with an O–O bond angle between 101.9 – 102.6°. These geometries are in good agreement with previous literature results for the ozonolysis of other alkenes,^{20–22,60,61} suggesting parent hydrocarbon structure has little influence on POZ geometry.²²

For each addition pathway, the two TSs leading to different POZ conformers have very similar energies, such that channels essentially contribute equally to POZ formation. Furthermore the chemically activated POZs face low interconversion barriers of 9.7/10.2 kJ mol⁻¹ (**TS12**) for **POZ1a** and **POZ1b** and 11.9/13.8 kJ mol⁻¹ (**TS34**) for **POZ2a** and **POZ2b**, such that the adduct populations will interconvert rapidly, readily assuming a microcanonical equilibrium independent of their initial ratios.

The addition process is highly exothermic with POZs lying over 166 kJ mol⁻¹ lower in energy compared to the free reactants (Table 1). The nascent energy is retained in the POZ ring structure, resulting in prompt decomposition through

homolytic cleavage of the C–C and one of the O–O bonds which forms, in the case of asymmetrically substituted α -phellanderne, pairs of CI products. Ring opening occurs in competition with collisional stabilisation with the bath gas, however, the high nascent energy content combined with low barriers for POZ decomposition ($< 70 \text{ kJ mol}^{-1}$) leads to near-complete prompt POZ decomposition.^{25,62}

Ring opening of **POZ1a** proceeds via **TS1a** and **TS2a**, the former lying 19.5 kJ mol^{-1} lower in energy such that **CI1a** is likely the only relevant reaction product. Despite negligible contributions from **CI2a** to the product distribution, discussion of its degradation is included in this paper for mechanistic completion and interest. Ring breaking of **POZ1b** goes through either **TS1b** or **TS2b**, with the two TSs separated by 4.5 kJ mol^{-1} . Therefore **CI2b** will be the favoured Criegee structure, although **CI1b** will also contribute to the product distribution.

Ring opening of **POZ2a** and **POZ2b** yields pairs of TSs that are quite similar in energy, a result of similar (mono-)substitution present on either side of the ozonide moiety. **POZ2a** decomposes through either **TS3a** ($-109.8 \text{ kJ mol}^{-1}$) or **TS4a** ($-112.0 \text{ kJ mol}^{-1}$), producing the Criegees **CI3a** and **CI4a** respectively. The energy difference between these two TSs is within the error threshold of the theoretical methods used in this study, and so no comment can be made on the relative formation ratios of these two CIs. Ring opening of **POZ2b** proceeds through either **TS3b** ($-97.8 \text{ kJ mol}^{-1}$) or **TS4b** ($-97.8 \text{ kJ mol}^{-1}$) to yield equivalent amounts of **CI3b** and **CI4b**. Overall similar formation rates of **CI3** and **CI4** are

expected, indicating that the adjacent π -bond has little impact on **POZ2a** and **POZ2b** decomposition.

For the eight CIs investigated, energies ranged from 210.0 – 233.0 kJ mol⁻¹ below that of the starting reactants. Given that ring-opening reactions in the POZ does not segment the molecule as a whole, all nascent energy is retained in the structure resulting in highly chemically activated CIs. As found for other CIs,^{25,63,64} the interconversion of CIs between conformers (e.g. **CI1a** and **CI1b**) is slow, with barriers for (pseudo)rotating the terminal oxygen in excess of 150 kJ mol⁻¹. Geometries show that these high barriers are the result of a double bond existing between carbon and oxygen in the dominant wavefunction for the substitute CIs; with these structures better described as closed-shell, charge-separated zwitterions rather than biradical species.⁶⁵ When compared to the unimolecular decomposition pathways in Figures 5 – 8, conversion between CI conformers is extremely uncompetitive and can be safely neglected.

Thus far, the entire discussion has focussed on the singlet PES. However decomposition of POZs results in highly energetic CI biradicals forming, thus the possibility of inter-system crossings (ISCs) must be considered. Ozone's ground state wavefunction is known to show singlet character, with the lowest lying triplet state located around 100 kJ mol⁻¹ above the ground state.^{66,67} CIs are isoelectronic to ozone, with an analogous singlet ground state.⁶⁵ However the vibrationally excited POZs can migrate onto the triplet PES and form stable minima through cleavage of an O–O bond, with the ISC induced by strong spin-orbit coupling effects (S.4, ESI).^{68,69} It is then possible to form triplet CIs through

subsequent decomposition on the triplet PES. Such a pathway was found to be energetically unfavourable. Whilst an initial ISC onto the triplet surface may occur, as it is competitive with forming a singlet TS, upon cleavage of the C–C bond migration back onto the singlet surface is energetically favoured. In this sense, the triplet surface may act as an alternative pathway to forming singlet TSs. Nevertheless for the chemically activated POZs, the energy difference between the singlet TS and the triplet POZ is unlikely to have a large influence on the relative state density of these two kinetically critical points, resulting in a low probability of transition onto the triplet surface. Subsequent unimolecular reactions of the CIs is well-described using a restricted, closed-shell formalism, with only the bis(oxy) biradicals formed during dioxirane dissociation thought able to undergo an ISC onto the triplet PES. Such a transition is not investigated in this work, although results are expected to be similar to the findings of Nguyen *et al.*^{25,63} for β -pinene and β -caryophyllene, to which the reader is referred for further discussion.

3.2 Unimolecular reactions of the CIs

The fate of chemically activated CIs depends on their incipient energy, with unimolecular reactions occurring in competition with collisional stabilisation. For endocyclic alkenes such as α -phellandrene, where all of the nascent energy is retained in the tethered products, stabilisation requires multiple collisions.⁷⁰ The CIs, stabilised or chemically activated, can undergo unimolecular decomposition through pathways well established in the literature^{5,19}; including H-migration to form unsaturated hydroperoxides (hydroperoxide channel), cyclisation to dioxirane intermediates (ester or ‘hot’ acid channel), and internal ring-closure

reactions to yield secondary ozonides (SOZs) or cyclic peroxides (Figures 5 – 8). Stabilised CIs can additionally partake in bimolecular reactions with available atmospheric species (e.g. H₂O, NO₂, SO₂, aldehydes, carboxylic acids), which is uncompetitive for chemically activated CIs.^{19,70,71}

3.2.1 SOZ formation

Energetically, internal ring closure with the adjacent carbonyl group to yield a SOZ is the most favourable unimolecular reaction for all CIs derived from α -phellandrene, with barriers ranging from 17.6 – 60.0 kJ mol⁻¹. These values are consistent with the low barriers calculated for the sesquiterpene β -caryophyllene,⁶³ demonstrating that ring strain for monoterpenes with 6 carbons in the product ring is not detrimental to internal cyclization. However entropically SOZ formation is unfavourable. This is because a linear precursor forms a bicyclic TS, reducing the degrees of freedom for internal rotation into vibrational modes.^{62,63} For chemically activated CIs, entropic hindrance reduces the competitiveness of SOZ formation with respect to other unimolecular pathways, with high energy content enabling significantly looser TSs to dominate the chemistry. However the low energy barrier likely makes SOZ formation important, if not the dominant unimolecular channel for stabilised CIs formed from α -phellandrene ozonolysis.

For the CIs derived from **POZ1**, Figures 5 and 6 show both **CI1a** and **CI2b** cyclize to **SOZ1c**, facing barriers of 56.8 and 24.2 kJ mol⁻¹ through **TS1c** and **TS2f** respectively, whilst **C1b** and **CI2b** rearrange to **SOZ1f** through **TS1f** and **TS2c**, facing barriers of 27.0 and 17.6 kJ mol⁻¹ respectively. Meanwhile for CIs derived

from **POZ2** decomposition, Figures 7 and 8 show both **CI3a** and **CI4b** rearrange to **SOZ3c**, overcoming barriers of 60.1 (**TS3c**) and 31.3 kJ mol⁻¹ (**TS4f**) respectively, whilst **CI3b** and **CI4a** cyclize to **SOZ3e** through **TS3e** and **TS4c**, facing barriers of 39.0 and 27.9 kJ mol⁻¹ respectively. The barriers for SOZ formation from **CI1a**, **CI2a**, **CI2b**, **CI4a** and **CI4b** are significantly lower in energy compared to other accessible unimolecular decomposition channels (> 20 kJ mol⁻¹), indicating that SOZ formation likely dominates when these CIs are thermalised. For **CI1b**, **CI3a** and **CI3b**, other competitive pathways exist which are discussed in later sections. The pairs of SOZs formed are conformational isomers, and can interconvert rapidly through low barriers (**TS1k**, **TS3i**, 9 – 16 kJ mol⁻¹) such that a microcanonical equilibrium will likely be established independent of their nascent ratios.

The atmospheric fate of SOZs is largely unknown, with decomposition to acids and esters through simultaneous C–C and C–O bond cleavage investigated. The decomposition product is found to be dependent on the orientation of the bridging peroxide group, with **SOZ1c** rearranging to **ESTER1b** and **ACID1** through barriers of 127.5 (**TS1l**) and 165.9 kJ mol⁻¹ (**TS1m**), while **SOZ1f** decomposes to **ESTER1a** and **ESTER1c** over barriers of 191.1 (**TS1o**) and 178.0 kJ mol⁻¹ (**TS1n**) respectively (Figure 5). Given the low barrier of interconversion between the two SOZs (**TS1k**), it is likely that the majority of decomposition will occur through the lowest barrier channel, yielding **ESTER1b**.

For the other set of SOZs, **SOZ3c** was found to decompose to **ACID3b** and **ESTER3a** through **TS3j** and **TS3k**, facing barriers of 169.5 and 127.4 kJ mol⁻¹

respectively, whilst **SOZ3e** decomposes through barriers of 169.2 (**TS3l**) and 137.8 kJ mol⁻¹ (**TS3m**) to yield **ACID3a** and **ESTER3b** respectively (Figure 7). The barriers for ester and acid formation are significantly different for both conformers of **SOZ3** (> 30 kJ mol⁻¹), with ester formation again the likely unimolecular decomposition product.

The high barriers of decomposition observed for α -phellandrene derived SOZs are consistent with what has been reported in the literature for ethylene⁷² and β -caryophyllene⁶³, confirming the stability of SOZs as first-generation products. Bimolecular reactions are therefore the likely degradation fate of α -phellandrene derived SOZs in the atmosphere, predominantly occurring through addition of OH radicals, NO₃ radicals, or O₃ to the remaining double bond.⁵

3.2.2 Hydroperoxide channel

The hydroperoxide channel is thought to be the major source of OH radicals in the ozonolysis mechanism of alkenes,^{5,19} and, when available, the major decomposition route for chemically activated CIs.⁷⁰ The conventional hydroperoxide channel is accessible for **CI1a**, **CI1b**, **CI2b** and **CI4b**, with barriers of 71.0 – 90.5 kJ mol⁻¹ observed for 1,4-H shifts through transition states **TS1d**, **TS1g**, **TS2g** and **TS4g**, yielding the vinylhydroperoxide intermediates **HP1d**, **HP1g**, **HP2g** and **HP4g** respectively.⁷³ The chemically activated intermediates dissociate promptly through a barrierless reaction channel, forming OH radicals, along with resonance-stabilised vinoxyl-like radicals **RAD1d**, **RAD1g**, **RAD2g** and **RAD4g**. For **CI2** and **CI4** the conventional mechanism can only proceed in the configuration where the outer oxygen of the Criegee moiety is *syn* to the alkyl

group. Meanwhile the configuration of **CI1** allows both conformers to access the traditional hydroperoxide channel, with abstraction of hydrogen from the methyl group through **TS1d** favoured over vinyl abstraction (**TS1g**).^{60,74,75}

For the remaining Criegee intermediates, **CI2a**, **CI3a**, **CI3b** and **CI4a**, the conventional hydroperoxide channel is inaccessible. In the *syn*-CI, **CI3b**, there are no available hydrogens in the 1,4-position for the conventional hydroperoxide channel to proceed. However due to the adjacent double bond, a low-lying, allyl-resonance stabilised TS can be accessed through a 1,6-hydrogen shift (Figure 7), a pathway that has no precedence in the literature. An analogous channel is also available for **CI1b**, which is outlined in Figure 9. A significant reduction in energy compared to conventional routes is observed, with **CI1b** needing to surmount a low barrier of 30.3 kJ mol⁻¹ to cross **TS1h**, whilst **CI3b** has to clear a barrier of 46.7 kJ mol⁻¹ through **TS3f**. Nevertheless, as the radical electron is still involved in the TS active site, allyl resonance is not in full effect until after the barrier has been cleared, at which point it drives the barrier down through the products **HP1h** and **HP3f**, with resultant loss of OH forming the resonance stabilised radicals **RAD1h** and **RAD3f**. Geometry in the radical products suggests a mixture of all canonical structures. The newly proposed hydroperoxide pathway is recognisably akin to the advantageous 1,6-H migration channels found for alkenylperoxy radicals, where allyl-resonance stabilisation significantly lowers barrier heights compared to other abstraction pathways.⁷⁶⁻⁷⁸ The energetic advantage provided by the allyl-resonance stabilised 1,6-H migration channel results in it being the only hydroperoxide channel accessed by **CI1b** and **CI3b**. The reduction in energy also makes the

hydroperoxide channel for these CIs competitive with SOZ formation, such that a 1,6-H migration may additionally be a competitive pathway for thermalised **CI1b** and **CI3b** biradicals. These results are likely to extend to other structurally similar terpenes (e.g. α -terpinene, ocimene, safranal).

For the *anti*-CIs, **CI2a**, **CI3a** and **CI4a**, a 1,4-H shift is geometrically not possible, with 1,3-H migrations found to have high barriers in excess of 120 kJ mol⁻¹ (S.5, ESI), making these reactions negligibly slow. The high barriers are consistent with what has been calculated for other alkenes in the literature.^{63,79-81} In order to explain the formation of pinonic acid from the ozonolysis of α -pinene, Ma *et al.*¹³ proposed an alternate mechanism whereby the CI isomerises through an aldehydic hydrogen abstraction. Whilst uncompetitive with competing hydroperoxide pathways in **CI1a** and **CI3b** (S.5, ESI), the mechanism was found to provide an alternative hydroperoxide pathway with a lower barrier than 1,3-H migration for **CI4a** (Figure 8). The mechanism proceeds through a 1,8-H shift with the acyl hydrogen, over a barrier of 95.5 kJ mol⁻¹ through **TS4d**. Post-transfer, the product rearranges into a relatively stable, 6-membered ring containing species **HP4d**. Driven by overall reaction exothermicity, decomposition through barrierless loss of OH proceeds, yielding the alkoxy radical **RAD4d**. Subsequent decay can occur through breaking adjacent C-C σ -bonds, rupturing the ring to form radicals **RAD4j** and **RAD4k**, along with OH radicals. The TSs lie 27.1 kJ mol⁻¹ apart however, with formation of the acyl radical **RAD4k** through **TS4k** overwhelmingly favoured, due to superior stability of the acyl radical compared to the alkyl radical^{82,83} and resonance stabilisation with the adjacent π -bond.

374

375 The principle of acyl abstraction was applied to **CI2a**, where there is no adjacent
376 aldehyde group, with a 1,9-H transition from the methyl group (**C1**) found to
377 have a barrier of 102.2 kJ mol⁻¹ through **TS2d**. Such a reaction has no
378 precedence in the literature, with the structure of α -phellandrene enabling re-
379 arrangement into a stable 7-membered ring **HP2d** to occur. Driven by overall
380 reaction exothermicity, decomposition through barrierless loss of OH proceeds,
381 yielding the alkoxy radical **RAD2d**. Subsequent decay can occur through ring-
382 breaking of either adjacent C-C σ -bond, with transition states **TS2j** and **TS2k**
383 energetically indiscernible at G4(MP2) resolution. Consequently similar yields of
384 radicals **Rad2j** and **Rad2k** are expected through this mechanism.

385

386 The radicals formed through the various hydroperoxide channels are rapidly
387 stabilised by the addition of an oxygen molecule in the atmosphere, and can
388 further decompose to a large number of low volatility products.^{35,84}

389

390 3.2.3 Ester or 'hot' acid channel

391 The ester or 'hot' acid channel first involves the formation of a dioxirane through
392 cyclisation of the CIs, after clearing barriers of 71 – 98 kJ mol⁻¹ for the *syn*-
393 conformers through **TS2h**, **TS3g** and **TS4h**, and 62 – 70 kJ mol⁻¹ for the *anti*-
394 conformers through **TS2e**, **TS3d** and **TS4e**. For **CI1** where conformational
395 distinction is ambiguous; **CI1a** and **CI1b** had barriers of 87.2 (**TS1e**) and 74.0 kJ
396 mol⁻¹ (**TS1i**) to overcome respectively. The large difference in observed barrier
397 heights is due to steric hindrance in the *syn*-conformers. Indeed the largest
398 differences between conformer barriers (> 24 kJ mol⁻¹) are found in **CI2** and **CI4**,

where the Criegee moiety is adjacent to the isopropyl group. For terminal CIs, it has widely been discussed in the literature that *syn*-CIs favour the hydroperoxide channel, whilst *anti*-CIs (which cannot access the traditional hydroperoxide channel) favour the ester or 'hot' acid channel (Vereecken and Francisco⁷⁰ and references therein). It therefore appears that the availability of a 1,4-hydrogen is not the sole reason why the hydroperoxide channel is favoured in the *syn*-conformer; rather it is that the ester or 'hot' acid channel is significantly hindered, rendering it uncompetitive. Indeed this is the trend observed for **CI2**, **CI3** and **CI4**, where the hydroperoxide channel is strongly favoured for the *syn*-conformer (**CI2b**, **CI3b** and **CI4b**) and ester or 'hot' acid channel for the *anti*-conformer (**CI2a**, **CI3a** and **CI4a**). The ester or 'hot' acid channel for **CI2a**, **CI3a** and **CI4a** yields **DIO2**, **DIO3** and **DIO4** respectively. Interestingly dioxirane formation from **CI3a** is competitive with SOZ formation, with thermalised **CI3a** biradicals expected to contribute non-negligibly to the **DIO3** budget. The hydroperoxide channel is favoured for both conformers of **CI1**, with trivial amounts of **DIO1** expected through the ester or 'hot' acid channel.

The dioxiranes formed are comparatively stable, lying 75 – 105 kJ mol⁻¹ lower on the PES than the starting CIs. The general chemistry of dioxiranes is well described in the literature^{85,86}; and in non-atmospheric applications they are known as strong epoxidising agents. Chemically activated dioxiranes rupture the O–O bond, forming a singlet bis(oxy) biradical, which readily displaces a neighbouring substituent to form an acid or ester. In their systematic computational study on bis(oxy) biradical isomerisation reactions, Nguyen *et al.*⁶³ found that with two different alkyl substituents, both ester-forming

channels could be competitive, whilst for terminal bis(oxy) biradicals, H-atom migration would be dominant. Cremer *et al.*⁸⁶ also showed loss of CO₂ from smaller dioxiranes to be energetically favourable, however this process is thought to be insignificant in the larger α -phellandrene system, with the aforementioned isomerisations taken as the sole channel for dioxirane decomposition.

Migration of either substituent group in **DIO1** yields an ester, facing barriers of 149.6 (**TS1q**) and 108.9 kJ mol⁻¹ (**TS1p**) for **ESTER1a** and **ESTER1b** respectively. Meanwhile **DIO3** can promptly rearrange through **TS3n**, facing a barrier of 72.1 kJ mol⁻¹ to form **ESTER3a**, with the corresponding TS to **ACID3a** unable to be located on the B3LYP/6-31G(2df,p) PES. IRC calculations for each channel connected the TSs to both reactants and products, with no singlet bis(oxy) intermediate observed, contrary to other studies.^{25,63,86} Nevertheless high level CASPT2//CASSCF calculations by Nguyen *et al.*⁶³ have shown the singlet bis(oxy) intermediate to be thermally unstable, with a very low or negligible barrier to isomerization. The barriers for ester formation suggest that the neighbouring vinyl groups make better migrating groups than either methyl or hydrogen atoms, implying that electron density in the adjacent π -bond is able to stabilise the TS more effectively. Indeed the effect of olefin substituents was not considered in the investigation of Nguyen *et al.*⁶³. It is therefore tentatively proposed that when a dioxirane is adjacent to a vinyl group, ester formation involving the vinyl moiety is favoured.

Conventional TSs yielding acids and esters from **DIO2** and **DIO4** could not be located on the B3LYP/6-31G(2df,p) PES. Instead, re-arrangement into epoxides **EPOX2** and **EPOX4** was found to occur through **TS2i** and **TS4i** respectively, facing barriers of 75.7 and 63.6 kJ mol⁻¹. Epoxide formation from dioxiranes has precedence in the organic literature (Murray⁸⁵ and references therein), with bimolecular epoxidation having been subject to computational investigation.⁸⁷⁻⁹⁰ However this is the first time that unimolecular epoxidation by a dioxirane has been proposed as a decomposition pathway. As shown in Figure 10, with further discussion in the ESI (S.6), the TSs show the characteristic concerted spiro-type structure that is observed in bimolecular dioxirane epoxidation reactions.⁸⁷⁻⁹⁰ This spiro approach allows modest back bonding of the oxygen lone pair with the olefin π^* orbital. The conformations of both **CI2b** and **CI4b** allow attainment of the advantageous spiro TS without excessive ring strain or steric hindrance. Such a process is believed to be unfavourable for smaller conjugated systems such as isoprene, or systems where the olefin group is too far separated in space from the dioxirane such as in β -caryophyllene, as ring strain to achieve a spiro TS would be too high. Indeed the barriers for epoxidation are favourable with respect to the other dioxirane decomposition channels investigated in this study.

The non-radical first generation products formed through SOZ and ester or 'hot' acid channels have very high energy content, with overall reaction exothermicity in excess of 540 kJ mol⁻¹. If formed through excited channels, such high internal energy is sufficient for chemically activated unimolecular reactions to occur; with elimination of a CO₂ molecule facing barriers of over 290 kJ mol⁻¹ for the various acid and ester products (S.7, ESI). The high barrier heights for CO₂

elimination are consistent with what has been computed for smaller alkenes,^{91,92} β -pinene²⁵ and β -caryophyllene⁶³. Nevertheless the size and stability of the acid and ester products make it highly likely that they will be collisionally stabilised, preventing further unimolecular decomposition. The dioxiranes can also be collisionally stabilised but, under atmospheric conditions, thermal decomposition and rearrangement into esters/acids ultimately results.⁷⁰ The two epoxides formed are expected to be stable, with formation saturating the molecule thus slowing the rate of bimolecular decomposition. **EPOX2** and **EPOX4** are therefore likely to be thermalised by collisions with the bath gas, with relatively long lifetimes compared to other unsaturated first generation degradation products.

The thermalised high-molecular weight oxygenated products, including SOZs, acids, esters and epoxides, are all formed without loss of carbon from the α -phellandrene backbone, resulting in a significant reduction in species vapour pressure. The first generation products are therefore expected to partially condense in the atmosphere, contributing to SOA formation. The product distribution developed in this work can therefore go some way to explaining the high SOA yields that have been observed experimentally from α -phellandrene ozonolysis.³⁵

3.2.4 Cyclic peroxide formation

The residual double bond in α -phellandrene CIs enables another possible cyclisation reaction to occur for **CI1b** and **CI3b**, namely a 1,5-electrocyclisation reaction to a cyclic peroxide. The mechanism was first reported in Kuwata *et*

*al.*⁶⁰, who found a barrier for methyl vinyl carbonyl oxide cyclisation of 46 kJ mol⁻¹, with yields of 40 – 45% predicted. Low barriers of 47.3 and 42.5 kJ mol⁻¹ are similarly calculated for **CI1b** and **CI3b** respectively, through transition states **TS1j** and **TS3h**. Indeed geometries for the transition states **TS1j** and **TS3h**, and the products **CP1j** and **CP3h**, are akin to the isoprene analogues in Kuwata *et al.*⁶⁰, with the reaction showing all the same hallmarks of a monorotatory pericyclic process; that being significant rotation of the vinyl group out of its original plane (torsional angles of 137.0° and -72.2° for **TS1j**, and 65.5° and -140.9° for **TS3h**), significant lengthening of the double bonds (increases of 0.05 Å, 0.02 Å, 0.04 Å and 0.03 Å for the C=C and C=O double bond in **TS1j** and **TS3h**), and significant shortening of the single bond (decrease of 0.05 Å and 0.06 Å for **TS1j** and **TS3h**) compared to the starting CIs. This suggests that given the right configuration of functional groups, the process is independent of parent species – with a pair of conjugated double bonds the only prerequisite.

Compared to other unimolecular decomposition routes, the barriers observed for 1,5-electrocyclisation are low. However, as is the case for SOZ formation, cyclisation of a CI to a 5-membered ring is entropically unfavourable, with the reaction only likely to be competitive for thermalised CIs. For **CI1b**, both a hydroperoxide (**TS1h**) and SOZ forming channel (**TS1f**) lie approximately 20 kJ mol⁻¹ lower in energy (Figure 5), such that 1,5-electrocyclisation into **CP1j** is unlikely to be a major channel. Meanwhile 1,5-electrocyclisation of **CI3b** through **TS3h** lies 3.6 kJ mol⁻¹ higher than the SOZ forming channel (**TS3e**), and 4.1 kJ mol⁻¹ lower than the hydroperoxide forming channel (**TS3f**) (Figure 7). These

values are within the uncertainty of the computational methods used, with all three channels likely competitive during **CI3b** decomposition.

The high yields of cyclic peroxides predicted during the decomposition of isoprene⁶⁰ stems from a lack of competitive pathways. For α -phellandrene CIs both SOZ formation, which as an intramolecular pathway is unavailable for isoprene, and a resonance stabilised hydrogen shift, for which isoprene CIs do not have the necessary size, are competitive. Consequently the high yields of cyclic peroxides reported in Kuwata *et al.*⁶⁰ for isoprene are not expected to be replicated in the ozonolysis of α -phellandrene. The decomposition of **CP1j** and **CP3h** was not investigated in this work but, given the similarities observed with isoprene analogues, it is expected that they will undergo similar unimolecular decomposition pathways to form epoxides and dicarbonyls.⁶⁰

4. Conclusion

The gas-phase ozonolysis of α -phellandrene is studied theoretically for the first time using the high-level *ab initio* G4(MP2) thermochemical protocol. The eight addition channels of O₃ to the two double bonds in α -phellandrene were examined, with the lowest barriers existing for addition to the least substituted double bond. Subsequent decomposition of four primary ozonides to form eight distinct Criegee intermediates were studied, with the hydroperoxide and ester or 'hot' acid channels accessible for these chemically activated CIs, and internal ring closure reactions to form secondary ozonides and cyclic peroxides investigated. In general, entropically unfavourable reactions had the lowest barriers for reaction, with considerable SOZ formation expected for thermalised CIs. The

chemically activated CIs showed significant differences in their chemistries, however in general *syn*-CIs favoured the hydroperoxide channel and *anti*-CIs the ester or 'hot' acid channel. Interestingly, the cyclic conjugation present in α -phellandrene enables a favourable allyl-resonance stabilised 1,6-H migration to occur in **CI1b** and **CI3b** and unimolecular epoxide formation in the ester or 'hot' acid channel of **CI2** and **CI4**. These novel processes are competitive with conventional mechanisms, and are thus expected to be important in the ozonolysis of structurally similar compounds (e.g. α -terpinene, ocimene, safranal). Given the lack of attention α -phellandrene has received in the literature, the pathways and first generation products characterised in this study can be used to assist in the analysis of future laboratory studies, and guide mechanism development.

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Addition Pathway	$\Delta G_{298}(\text{TS})$	$\Delta G_{298}(\text{POZ})$
DB1a	46.8	-171.5
DB1b	45.7	-171.1
DB2a	38.7	-167.9
DB2b	37.6	-166.0
DB1a*	41.3	-175.0
DB1b*	41.3	-175.6
DB2a*	43.4	-167.9
DB2b*	46.1	-166.0

Table 1. Change in Gibbs free energy (ΔG_{298} , G4(MP2), in kJ mol⁻¹) with respect to free ozone and α -phellandrene for the 8 distinct initiation pathways possible in the ozonolysis of α -phellandrene. *Denotes attack from the face with the dashed red line in Figure 2.

Figure 1. Simplified mechanism showing the first stages of ozone addition to α -phellandrene, within conventional frameworks.

Figure 2. Preferred O_3 attack faces of α -phellandrene for the two double bonds.

Figure 3. Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol^{-1}) outlining the initial steps of the PES for the ozonolysis of **DB1** in α -phellandrene. ΔG is with respect to the free reactants.

Figure 4. Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol⁻¹) outlining the initial steps of the PES for the ozonolysis of **DB2** in α -phellandrene. ΔG is with respect to the free reactants.

Figure 5. Schematic Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol⁻¹) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of **CI1**.

Figure 6. Schematic Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol⁻¹) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of **CI2**.

Figure 7. Schematic Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol⁻¹) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of **CI3**.

Figure 8. Schematic Gibbs-free energy profile (ΔG_{298} , G4(MP2), in kJ mol⁻¹) of the lowest lying singlet PES of the gas-phase unimolecular decomposition of **CI4**.

Figure 9. Newly proposed hydroperoxide channel for **Cl1b** through a 1-6 hydrogen shift, producing **HP1h** and **RAD1h**.

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864 **Figure 10.** Epoxidation geometries for **CI2b**, through **DIO2**, **TS2i** and **EPOX2**.