



Reaction Mechanism and Kinetics of Criegee Intermediate Formation in the Ozonolysis of a Marine Chlorinated Monoterpene: A Three-Channel Master-Equation Analysis

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Abstract: Atmospheric ozonolysis of halogenated monoterpenes from marine red macroalgae proceeds through pre-reactive complexes, primary ozonides, Criegee intermediates, and carbonyl products. Structure–activity relationship (SAR) schemes, such as that of Khan et al. (2022) for nineteen Plocamium-derived monoterpenes, return only a single rate coefficient per channel, with no information on intermediates, energy partitioning or pressure dependence. Here all three ozone-attack channels of Compound **1**, 5,6-dichloro-2-chloromethylene-6-methyl-octa-3,7-dienal (C₁₀H₁₁Cl₃O) — the terminal Δ^7 vinyl, the internal Δ^3 double bond, and the chloromethylene Δ^1 group — are characterized with a quantum-chemical/master-equation workflow (ω B97X-D3BJ/def2-TZVP; DLPNO-CCSD(T)/def2-TZVPP; ORCA 6.1; MESMER 7.1) on a single workstation. All three channels proceed over tight, first-order cycloaddition transition states to deep primary ozonides and on to chlorinated carbonyl + Criegee pairs. The internal Δ^3 cycloaddition, initially suspected to be barrierless along the single-bond approach coordinate, is shown by a synchronous two-bond scan, transition-state optimization and intrinsic-reaction-coordinate analysis to possess a genuine concerted ring-closure saddle (one imaginary mode, -310 cm^{-1}) at $+9.57\text{ kcal mol}^{-1}$ — the highest of the three entrance barriers, above the terminal Δ^7 ($+7.02$) and chloromethylene Δ^1 ($+6.67\text{ kcal mol}^{-1}$) channels. The resulting 298 K, 760 Torr rate coefficients are $k_{\Delta^7} = 2.50 \times 10^{-21}$, $k_{\Delta^1} = 1.45 \times 10^{-22}$ and $k_{\Delta^3} = 1.53 \times 10^{-23}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, giving a channel ordering $\Delta^7 > \Delta^1 > \Delta^3$ ($\approx 94 : 5 : 1$). This confirms the SAR/MCM picture of Khan et al. on the dominant site — the terminal Δ^7 vinyl — but reassigns the minor chemistry: the internal Δ^3 double bond, treated by SAR/MCM as the secondary site ($\sim 7\%$), is found to be the slowest channel ($\sim 1\%$), while the chloromethylene Δ^1 group not considered by SAR emerges as the true secondary channel ($\sim 5\%$). Notably, the ordering is not set by barrier height alone. Although Δ^1 has the lowest barrier, its tighter transition state (a smaller rovibrational partition function) makes it slower than Δ^7 , so the channel selectivity reflects a balance of entropic and enthalpic factors rather than barrier height in isolation. Pressure-dependent collisional stabilization of the primary ozonides — inaccessible to SAR — is significant at atmospheric pressure, with prompt Criegee yields of $\sim 28\%$ (Δ^7). Benchmarking the identical workflow against ethene ozonolysis reproduces the experimental barrier to within 0.4 kcal mol^{-1} (5.3 versus $\sim 4.95\text{ kcal mol}^{-1}$), indicating that the total rate, which lies about three orders of magnitude below the group-additivity SAR estimate, reflects overestimation by the SAR scheme for this chlorinated, conjugated substrate rather than an offset in the computed barriers.

Keywords: Criegee intermediate; ozonolysis; DLPNO-CCSD(T); master equation kinetics; halogenated monoterpene; secondary organic aerosol; branching ratio; transition-state entropy.

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1. INTRODUCTION

The chemical structures and bioactivities of over eighty acyclic halogenated monoterpenes, isolated from marine red macroalgae (Rhodophyta) of the genus *Plocamium* and related taxa, have been documented in the marine natural-product literature over the past four decades (1–3). These volatile species enter the marine boundary layer (MBL) directly when intertidal algae are exposed during low tide and indirectly through air–sea exchange, where they react with the principal tropospheric oxidants, the hydroxyl radical OH and ozone O₃ (4, 5). Owing to their conjugated and polyhalogenated structures, their atmospheric oxidation contributes to the formation of secondary organic aerosol, releases reactive halogens, and ultimately influences cloud-condensation-nuclei formation in the marine environment (5, 6).

The atmospheric importance of monoterpenes derives chiefly from their role as precursors of secondary organic aerosol (SOA). Biogenic volatile organic compounds are emitted at a global rate of approximately 1000 Tg yr^{−1}, roughly an order of magnitude greater than anthropogenic VOC emissions, and their oxidation by O₃, OH and NO₃ produces semi- and low-volatility species that condense to form SOA (6, 14). Global biogenic SOA production is estimated at tens of Tg yr^{−1}, with monoterpenes among the most important contributors after isoprene (6). SOA in turn affects the Earth's radiative balance both directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei (CCN) that modify cloud microphysics, lifetime, and albedo (6, 43). The marine boundary layer is a particularly sensitive setting for this chemistry: reactive halogen species released in the MBL account for an estimated 30% of local ozone destruction and 5–20% globally (41, 42), so the halogen-bearing oxidation products of marine monoterpenes feed directly into the coupled halogen–ozone–aerosol system that governs the oxidizing capacity of the remote marine atmosphere.

Within this picture, Criegee intermediates (carbonyl oxides, R₁R₂COO) occupy a pivotal position. Formed exclusively in the ozonolysis of alkenes, the stabilized fraction of these intermediates (sCI) is a potent oxidant of SO₂, converting it to SO₃ and hence to gas-phase H₂SO₄ — the key nucleating species in atmospheric new-particle formation (5, 39). Modeling studies constrained by field measurements have concluded that the sCI + SO₂ reaction can contribute as much as 33–46% of ground-level gas-phase sulfuric acid in VOC-rich environments (40). For halogen-substituted monoterpenes such as the *Plocamium*-derived compounds, this Criegee chemistry is essentially uncharacterized, even though the electron-withdrawing chlorine substituents are expected to alter both the branching into the Criegee channel and the subsequent fate of the carbonyl oxide.

Khan and co-workers (10) recently estimated the gas-phase rate coefficients of nineteen *Plocamium*-derived acyclic halogenated monoterpenes using the structure–activity relationship (SAR) approach of Atkinson and co-workers (11, 12). For the prototypical Compound **1** of the inventory, 5,6-dichloro-2-chloromethylene-6-methyl-octa-3,7-dienal (C₁₀H₁₁Cl₃O), the SAR analysis at 298 K returned $k_{\text{OH}} = 4.75 \times 10^{-11}$ and $k_{\text{O}_3} = 2.58 \times 10^{-18}$ cm³ molecule^{−1} s^{−1}, with the OH and O₃ oxidation channels assigned 94.8% and 5.2% of the total loss respectively. The SAR partitioning further distributes the total k_{O_3} over the three olefinic sites: the terminal Δ⁷ vinyl receives 93%, the internal Δ³ double bond 7%, and the chloromethylene Δ¹ group is not considered. As is shown in the present work, this distribution differs qualitatively from the topology of the underlying potential energy surface.

The SAR approach has clear practical strengths — computational efficiency, broad applicability, and the ability to deliver order-of-magnitude rate coefficients across structurally diverse families — and the qualitative conclusion of Khan et al. (10) that OH-initiated oxidation dominates the atmospheric fate of Compound **1** is well established (34). However, SAR is by construction limited to a single thermal rate constant per reaction at a single representative temperature, and the underlying group-additivity scheme is calibrated against sparsely substituted alkenes and dienes that exclude the densely halogenated, conjugated marine monoterpenes whose detailed reactivity is the focus of mechanistic atmospheric chemistry. Crucially, SAR provides no direct information on the reaction intermediates, the topology of the underlying potential energy surface, the energy content and stability of nascent primary ozonides, the competition between prompt and collision-stabilized pathways, or the structure and onward chemistry of the Criegee intermediates that drive much of the downstream tropospheric oxidation (4, 7, 27).

The aim of the present work is to establish and validate a quantum-chemical/master-equation workflow — assembled here entirely from open-source software — Avogadro 2 (15), Open Babel (16), and MESMER (8, 13) — together with ORCA, which is free of charge for academic use — as the computational foundation for a broader program on the Criegee chemistry of marine halogenated VOCs. The present study applies the workflow to all three ozonolysis channels of Compound **1**: the terminal Δ⁷ vinyl cycloaddition (designated Channel 1), the internal Δ³ double-bond cycloaddition (Channel 2), and the chloromethylene Δ¹ cycloaddition (Channel 3). All three proceed over tight, first-order cycloaddition transition states; for the internal Δ³ bond, locating that saddle point required a synchronous two-bond reaction coordinate, because a relaxed single-bond approach scan had initially suggested — misleadingly — a barrierless entry. The channels differ in their Criegee products, which range from the unsubstituted CH₂OO to substituted

carbonyl oxides specific to halogenated marine compounds.

The remainder of this paper is organized as follows. Section 2 describes the workflow, including the rationale for each methodological choice (Section 2.1), the construction of the three-channel reaction model (Section 2.2), and the parametrization of the master-equation simulations (Section 2.3). Section 3 presents the resulting potential energy surfaces, microcanonical and phenomenological rate coefficients, pressure dependence, and channel branching, and compares the present analysis with the Khan et al. (10) SAR baseline. Section 4 summarizes the main findings and outlines the application of the same workflow to the OH-initiated chemistry of Compound 1 and to the remaining Plocamium-derived monoterpenes.

2.1. Methodological workflow and rationale

The full computational workflow used in the present work is summarized schematically in Figure 1. The five stages of the pipeline — molecular construction, electronic structure, cross-validation, master-equation kinetics, and atmospheric interpretation — together resolve a complete elementary-step mechanism for each of the three ozonolysis channels: stationary-point geometries, ZPE-corrected energetics, microcanonical rate coefficients, pressure-dependent phenomenological rate constants, Arrhenius parameters, and channel branching. The molecular-construction (Avogadro 2, Open Babel) and master-equation (MESMER) stages use open-source packages, while the electronic-structure stage (ORCA) uses software distributed free of charge for academic use. All calculations reported in this work were performed on a single Dell Precision 7920 Tower workstation; no high-performance computing resource was required.

2. COMPUTATIONAL METHODS

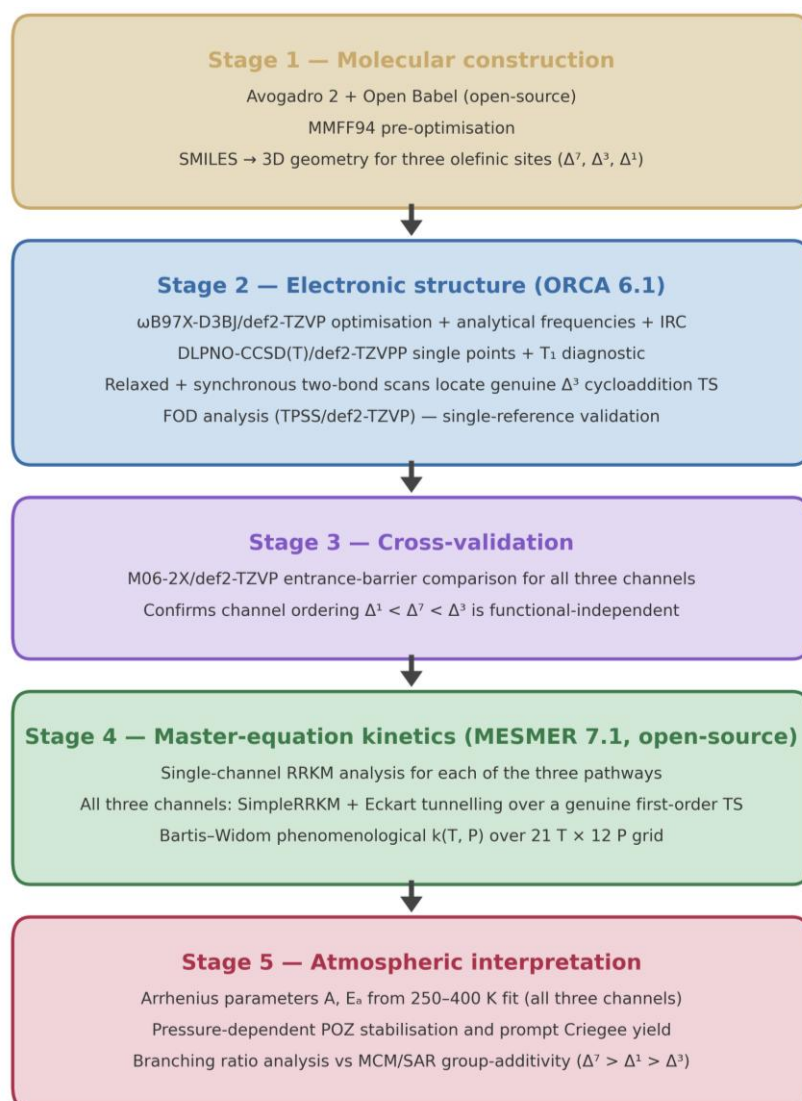


Figure 1: Computational workflow used in the present work. The five stages are implemented with Avogadro 2 + Open Babel (Stage 1), ORCA 6.1 (18,19) (Stages 2 and 3), and MESMER 7.1 (Stage 4); Stage 5 collects the atmospheric interpretation.

2.2. Choice of electronic-structure methods

Initial three-dimensional geometries for the three olefinic attack sites were assembled in Avogadro 2 with Open Babel and pre-optimized at the MMFF94 (17) molecular-mechanics level before quantum-chemical refinement. The choice of ω B97X-D3BJ/def2-TZVP (20, 21, 22) as the optimization and frequency level reflects three considerations. First, ω B97X-D3BJ is a long-range-corrected hybrid functional with D3 Becke-Johnson damping for dispersion, which is essential for the description of pre-reactive complexes between alkenes and O_3 and for the long-range correlation around the primary-ozonide ring. Second, the def2-TZVP basis set provides a converged description of the polarization function space around carbon, oxygen and chlorine without the computational cost of quadruple-zeta basis sets. Third, the combination is well-established as a reliable optimization level for ozonolysis stationary points in the recent computational atmospheric-chemistry literature (7, 9). In all hybrid-DFT steps, the Hartree-Fock exchange was evaluated using the chain-of-spheres (COSX) approximation as implemented in ORCA (23). Analytical harmonic frequencies are computed at the same level on every optimized geometry. To verify that the optimized structures correspond to the lowest-energy conformers, a systematic conformer-rotamer ensemble search was performed for the conformationally flexible stationary points — the three primary ozonides and the open-chain carbonyl and Criegee products — using the CREST conformer-sampling program (49) with the GFN-FF force field (50), retaining all conformers within 6 kcal mol⁻¹; the lowest-energy conformer of each species was then re-optimized at the ω B97X-D3BJ/def2-TZVP level and adopted where it lay below the original structure (Section 3.6). This conformational sampling was applied to the minima — the flexible primary ozonides and the open-chain carbonyl and Criegee products; the three cycloaddition transition states were not subjected to ensemble sampling and were each optimized from a single, chemically reasonable structure (see Section 3.6).

Single-point energies on the optimized geometries are refined at the DLPNO-CCSD(T)/def2-TZVPP level (24, 25) with TightPNO settings. DLPNO-CCSD(T) recovers nearly the full canonical CCSD(T) accuracy at a small fraction of the computational cost (24), with the def2-TZVPP basis chosen to balance basis-set completeness against cost (26) and provides a direct estimate of single-reference reliability via the T_1 diagnostic (32). The energetics are additionally cross-validated against an independent method, the M06-2X meta-hybrid density functional (28). Because DLPNO-CCSD(T) (a wavefunction-based coupled-cluster treatment) and M06-2X (a parametrized exchange-correlation functional) rest on fundamentally different approximations, their agreement on the rate-controlling barriers is far stronger evidence that those barriers are physically meaningful than either method could provide alone — which matters here because no experimental rate coefficient exists for

Compound 1 against which to calibrate. For all closed-shell species relevant to the three channels, the T_1 diagnostic falls below 0.025; the Criegee intermediates return elevated values (CH₂OO, T_1 = 0.042; the substituted Criegee of Channel 2, T_1 = 0.024; the chlorinated Criegee ClCHOO of Channel 3, T_1 = 0.035), consistent with the well-documented biradical/zwitterionic character of carbonyl oxides (33). A fractional-occupation-number weighted electron density (FOD) analysis (44), carried out at the default electronic temperature of 5000 K, on the Channel 1 retro-cycloaddition transition state and on CH₂OO returned N_{FOD} values of 0.47 e and 0.24 e respectively, both well within the single-reference range, confirming that the elevated T_1 diagnostic of the Criegee intermediates reflects dynamic rather than static correlation. The DLPNO-CCSD(T) energies of the Criegee intermediates themselves should nonetheless be regarded as carrying a somewhat larger uncertainty than those of the closed-shell minima, as is generic for carbonyl oxides; this does not propagate into the computed rate coefficients, because the Criegee intermediates are formed in the irreversible, kinetically downstream retro-cycloaddition step and their energies do not enter the rate-determining entrance kinetics. The M06-2X/def2-TZVP (28) cross-validation is performed for all three channels to test the functional dependence of the energetics. The two methods agree closely on the rate-controlling entrance barriers (Channel 1, +7.02 versus +5.01; Channel 3, +6.67 versus +4.84; Channel 2, +9.57 versus +7.39 kcal mol⁻¹ at DLPNO+ZPE versus M06-2X+ZPE), each functional placing the internal Δ^3 saddle highest and the two terminal-type saddles within ~ 0.4 kcal mol⁻¹ of one another; the cycloaddition step is therefore robust to the choice of functional both in absolute barrier height (within ~ 2 kcal mol⁻¹) and, more importantly, in the relative ordering of the three channels. The post-barrier primary-ozonide wells are systematically deeper at M06-2X (by ~ 11 – 13 kcal mol⁻¹; e.g. Channel 2, -58.87 versus -70.61 kcal mol⁻¹), so the well depth is the more functional-sensitive quantity; because these deep, kinetically irreversible wells do not enter the rate expression, this sensitivity does not affect the computed rate coefficients. Both columns of Table 1 are reported on a common basis, each including the ω B97X-D3BJ zero-point correction.

2.3. Reaction model and channel selection

The target molecule is Compound 1 of the marine halogenated-monoterpene inventory of Khan et al. (10): 5,6-dichloro-2-chloromethylene-6-methylocta-3,7-dienal (C₁₀H₁₁Cl₃O). The molecule possesses three olefinic moieties: the terminal Δ^7 vinyl group, the internal Δ^3 double bond, and the chloromethylene Δ^1 group conjugated to the aldehyde. The three sites differ markedly in their expected reactivity towards O_3 , and all three are characterized in the present work.

The three channels of the reaction model, illustrated in Figure 2, are: (Channel 1, Δ^7) the cycloaddition

of O_3 at the terminal Δ^7 vinyl group through TS_{Ch1} to the primary ozonide POZ_{Ch1} , followed by retro-cycloaddition through $retroTS_{Ch1}$ to a C_9 chlorinated carbonyl ($C_9H_9Cl_3O_2$) and the unsubstituted Criegee intermediate CH_2OO ; (Channel 2, Δ^3) the concerted cycloaddition at the internal Δ^3 double bond through TS_{Ch2} (+9.57 kcal mol⁻¹), to POZ_{Ch2} and a chlorinated C_4 enedial ($C_4H_3ClO_2$) + substituted C_6 Criegee pair; and (Channel 3, Δ^1) the cycloaddition at the chloromethylene Δ^1 group through TS_{Ch3} to POZ_{Ch3} , then through $retroTS_{Ch3}$ to a C_9 2-oxo-carbonyl and the chlorinated Criegee intermediate $ClCHOO$. IRC calculations confirmed the correct connectivity of all located transition states (TS_{Ch1} , TS_{Ch3} and the concerted internal-cycloaddition transition state TS_{Ch2} , together with the three retro-cycloaddition transition states; the Δ^3 entrance saddle was confirmed to connect the pre-reactive region to the primary ozonide POZ_{Ch2}).

An important methodological note concerns Channel 2. Relaxed scans along a single intermolecular $C\cdots O_3$ approach coordinate for the internal Δ^3 double bond initially exhibited monotonic energy descent toward a shallow van der Waals complex at -2.93 kcal mol⁻¹ below the separated reactants, with no first-order saddle point along that coordinate; taken alone, this behavior would suggest a barrierless entry. This single-coordinate scan, however, does not describe the concerted ring closure: ozone cycloaddition forms two $C\cdots O$ bonds, and the true reaction coordinate is the synchronous shortening of both contacts. A synchronous two-bond scan, in which both $C\cdots O$ distances were stepped together, was therefore constructed and revealed a clear energy maximum above the pre-complex, rather than the monotonic descent seen along the asynchronous coordinate. Starting from this maximum, an unconstrained transition-state optimization ($\omega B97X-D3BJ/def2-TZVP$) converged to a genuine first-order saddle point, TS_{Ch2} , characterized by a single imaginary frequency of -310.02 cm⁻¹ whose normal mode corresponds to the concerted two-bond ring closure. An intrinsic-reaction-coordinate (IRC) calculation initiated from TS_{Ch2} descended on one side into the deep primary-ozonide well POZ_{Ch2} and on the other side back toward the pre-reactive (van der Waals / separated-reactant) region, confirming that TS_{Ch2} is the cycloaddition transition state connecting reactants to POZ_{Ch2} . At the DLPNO-CCSD(T)/def2-TZVPP // $\omega B97X-D3BJ/def2-TZVP$ level, the electronic barrier of TS_{Ch2} is +7.81 kcal mol⁻¹ relative to separated reactants; adding the $\omega B97X-D3BJ$ zero-point correction ($\Delta ZPE = +1.76$ kcal mol⁻¹) gives a ZPE-corrected entrance barrier of +9.57 kcal mol⁻¹. The internal Δ^3 channel therefore possesses the highest of the three entrance barriers

— above the terminal Δ^7 (+7.02) and chloromethylene Δ^1 (+6.67 kcal mol⁻¹) cycloadditions — and is treated in the master-equation analysis on exactly the same footing as the other two channels, as a tight, first-order cycloaddition transition state with Eckart tunneling. The earlier impression of a barrierless entry is thus an artifact of probing only the asynchronous single-bond coordinate; the correct synchronous coordinate exposes a real, and in fact rate-limiting, saddle point. The need for a synchronous two-bond coordinate to locate the cycloaddition saddle of an internal double bond is consistent with earlier theoretical studies of alkene and terpene ozonolysis (48).

2.4. Master-equation kinetics

The three reactive networks are each propagated independently using the open-source master-equation solver MESMER 7.1 (8, 13) in single-channel mode. The single-channel approach is necessary because a combined three-well master-equation model — attempted at an earlier stage of this work — proved numerically ill-conditioned: the three deep primary-ozonide wells together produced a Bartsis-Widom eigenvalue spectrum in which the chemically significant eigenvalues did not cleanly separate from the internal energy-relaxation eigenvalues, and the resulting phenomenological rate coefficients deviated by many orders of magnitude from the corresponding single-channel values. The single-channel analysis sidesteps this numerical pathology and yields physically meaningful rate coefficients for each channel taken in isolation; the total ozonolysis flux is then constructed by summation. This treatment is physically appropriate here because the three channels compete in parallel for the same reactant (Compound 1 + O_3): the branching among them is governed entirely by the relative rates of the three independent bimolecular entrance steps from the common reactant, not by any coupling between the primary-ozonide wells, which are separated by very high effective barriers (the retro-cycloaddition transition states) and do not interconvert. The ill-conditioning of the combined model was therefore a numerical artifact of the eigenvalue analysis rather than a sign of genuine inter-well chemistry, and the branching is correctly recovered as the ratio of the single-channel entrance rate coefficients. For each channel, the reactant entry is treated as an explicit bimolecular association under the SimpleRRKM microcanonical formulation, and the POZ retro-cycloaddition as an irreversible unimolecular dissociation. Phenomenological, temperature- and pressure-dependent rate coefficients are extracted from the master-equation matrix following Bartsis-Widom analysis (31).

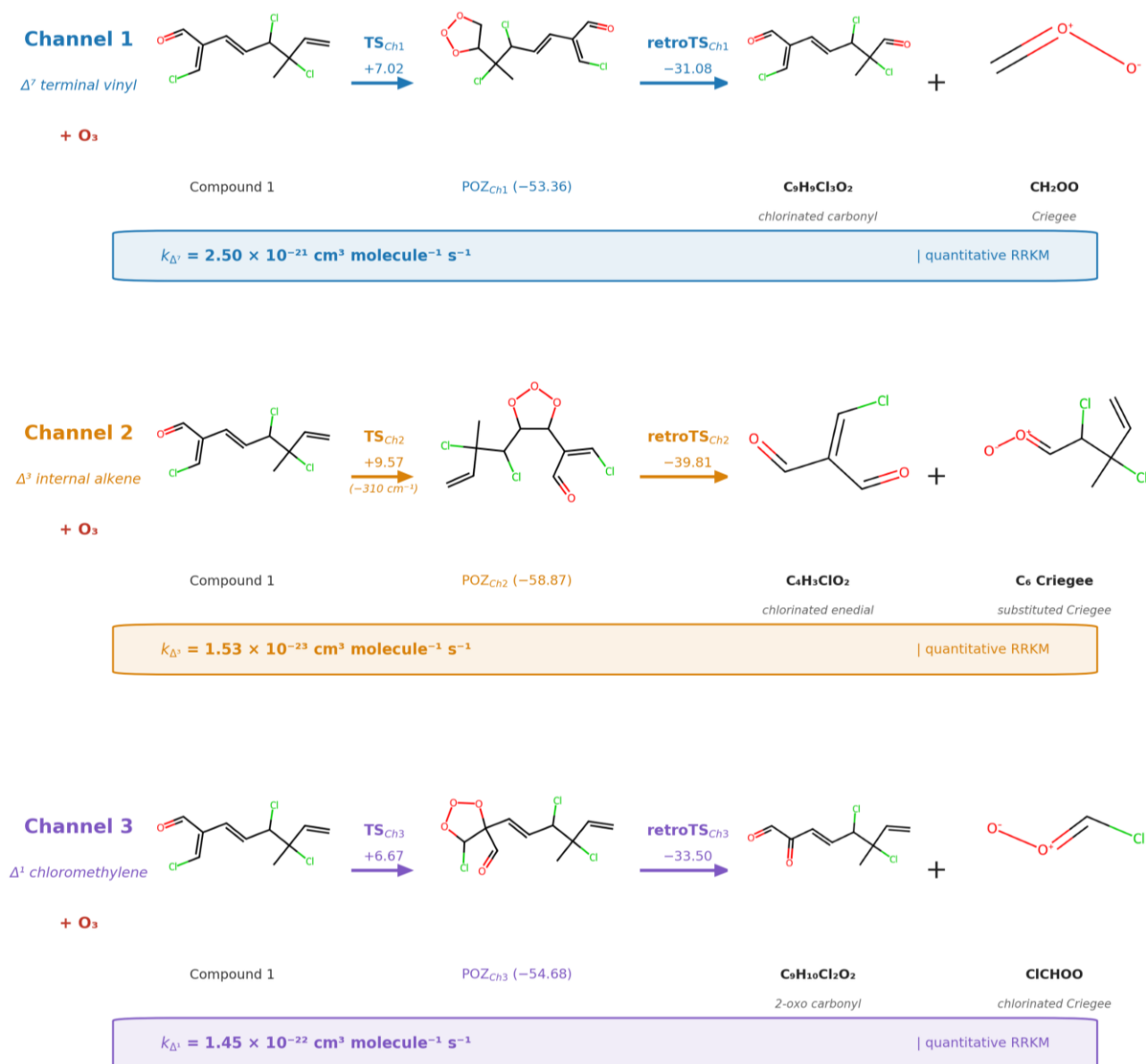
Three-channel ozonolysis mechanism of Compound 1 (C₁₀H₁₁Cl₃O)

Figure 2: Three-channel ozonolysis mechanism of Compound 1. Channel 1 (Δ^7 , terminal vinyl): bimolecular cycloaddition over TS_{Ch1} (+7.02 kcal mol⁻¹) to POZ_{Ch1}, then retro-cycloaddition to a C₉ chlorinated carbonyl + CH₂OO. Channel 2 (Δ^3 , internal): concerted cycloaddition over TS_{Ch2} (+9.57 kcal mol⁻¹, one imaginary mode -310 cm⁻¹) to POZ_{Ch2}, then to a (C₆ Criegee + chlorinated C₄ enedial (C₄H₃ClO₂)) pair. Channel 3 (Δ^1 , chloromethylene): cycloaddition over TS_{Ch3} (+6.67 kcal mol⁻¹) to POZ_{Ch3}, then to a C₉ 2-oxo-carbonyl + ClCHOO.

Eckart tunneling corrections (30) are applied to the cycloaddition and retro-cycloaddition transition states of all three channels, each of which is now represented by a genuine first-order saddle point. Because all three saddles correspond to heavy-atom (C...O bond-forming) motion, the tunneling corrections are modest (correction factors within roughly 1.1–1.5 at 298 K) and do not affect the channel ordering. Densities and sums of states are computed via the classical-rotor approximation with

an energy-grain size of 100 cm⁻¹. Collisional energy transfer is modeled via the single exponential-down probability function with $\langle \Delta E \rangle_{\text{down}} = 225 \text{ cm}^{-1}$ in an N₂ bath gas (29). The same temperature × pressure grid as in the Channel 1 analysis is retained: twenty-one temperatures (250–400 K) at 760 Torr and twelve pressures (50–5000 Torr) at 298.15 K.

3. RESULTS AND DISCUSSION

3.1. Potential energy surfaces

Table 1 summarizes the ZPE-corrected DLPNO-CCSD(T) relative energies of the stationary points of all three ozonolysis channels, referenced to the separated reactants $C_{10}H_{11}Cl_3O + O_3$. Each tabulated minimum returned zero imaginary frequencies, and each tabulated transition state returned exactly one imaginary frequency. All three channels proceed over tight, first-order cycloaddition transition states. The terminal Δ^7 and chloromethylene Δ^1 saddles have similar barrier heights (+7.02 and +6.67 kcal mol⁻¹) and similar imaginary frequencies (−296.36 and −323.12

cm⁻¹), reflecting the closely related electronic structure of the two terminal-type cycloadditions. The internal Δ^3 cycloaddition, accessed through the concerted synchronous-ring-closure saddle TSCh2 (imaginary frequency −310.02 cm⁻¹), has the highest entrance barrier of the three at +9.57 kcal mol⁻¹. All three primary ozonides lie in deep wells (−53.36, −58.87, −54.68 kcal mol⁻¹ for Channels 1, 2 and 3, respectively), providing substantial internal energy to drive prompt retro-cycloaddition or, alternatively, to be removed by collisional stabilization.

Table 1: Zero-point-energy-corrected relative energies (kcal mol⁻¹) of the stationary points along the three ozonolysis channels of Compound 1 at the DLPNO-CCSD(T)/def2-TZVPP // ω B97X-D3BJ/def2-TZVP level, referenced to separated reactants. M06-2X+ZPE cross-validation values are listed for the principal stationary points of all three channels, on a common zero-point basis with the DLPNO column; entries not computed are marked (—). T_1 diagnostics are listed for closed-shell species and Criegee intermediates; the elevated T_1 values for the Criegee intermediates are discussed in Section 2.2. Imaginary frequencies are at the ω B97X-D3BJ/def2-TZVP level.

Stationary point	$\Delta E_{DLPNO+ZPE}$	$\Delta E_{M06-2X+ZPE}$	Imag. freq.	T_1
Reactants ($C_{10}H_{11}Cl_3O + O_3$)	0.00	0.00	—	—
Channel 1 (Δ^7)				
TS _{Ch1} (cycloaddition)	+7.02	+5.01	−296.36	0.015
POZ _{Ch1}	−53.36	−66.25	—	0.013
retroTS _{Ch1}	−31.08	−38.03	−546.61	0.014
Products ($C_9H_9Cl_3O_2 + CH_2OO$)	−54.26	−64.34	—	0.013/0.042
Channel 2 (Δ^3)				
TS _{Ch2} (cycloaddition)	+9.57	+7.39	−310.02	—
POZ _{Ch2}	−58.87	−70.61	—	0.013
retroTS _{Ch2}	−39.81	−45.40	−562.82	—
Products (C_6 Criegee + C_4 carbonyl)	−54.11	−65.52	—	0.024/0.016
Channel 3 (Δ^1)				
TS _{Ch3} (cycloaddition)	+6.67	+4.84	−323.12	0.015
POZ _{Ch3}	−54.68	−65.29	—	0.012
retroTS _{Ch3}	−33.50	−39.23	−265.75	0.014
Products (C_9 2-oxo + ClCHOO)	−56.71	−66.42	—	0.013/0.035

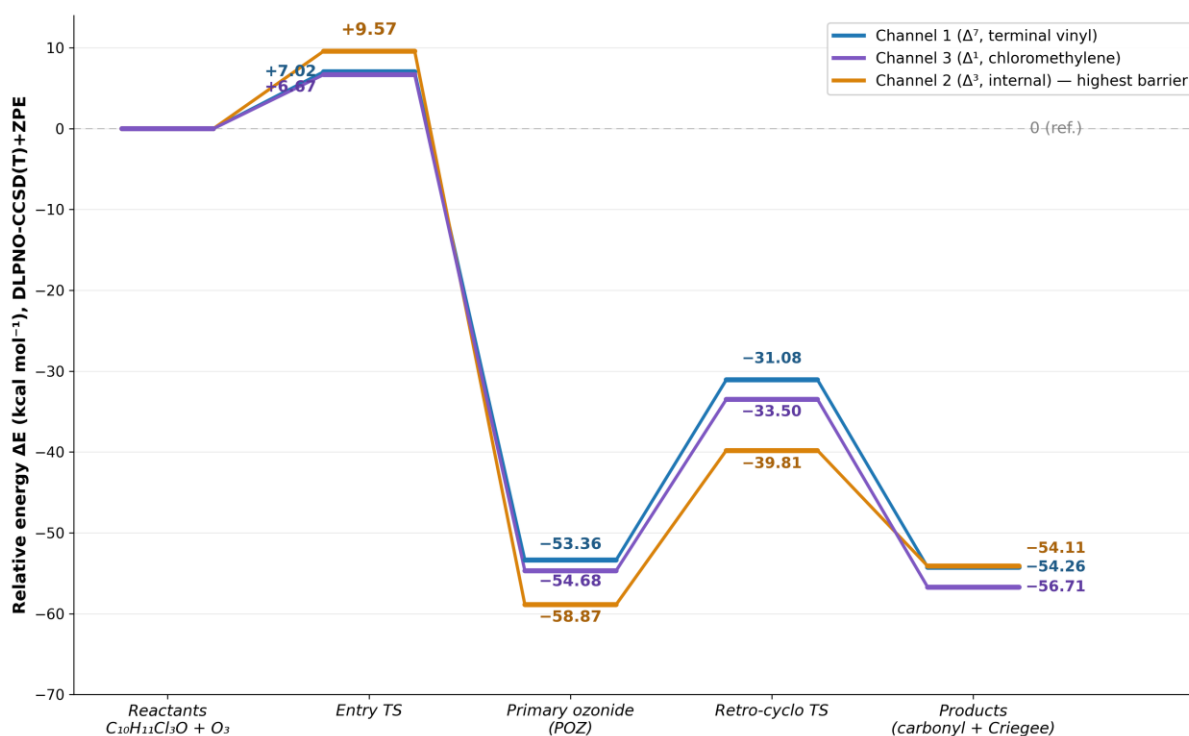


Figure 3: Zero-point-energy-corrected potential energy surfaces of the three ozonolysis channels of Compound 1, referenced to separated reactants $C_{10}H_{11}Cl_3O + O_3$. All three channels proceed over tight, first-order cycloaddition transition states to deep primary ozonides. Channels 1 (Δ^7 , blue) and 3 (Δ^1 , purple) pass over the terminal-type saddles at +7.02 and +6.67 kcal mol $^{-1}$ to wells at -53.36 and -54.68 kcal mol $^{-1}$. Channel 2 (Δ^3 , orange) passes over the concerted synchronous-ring-closure saddle TSCh2 (one imaginary mode, -310 cm $^{-1}$) at +9.57 kcal mol $^{-1}$ — the highest entrance barrier of the three — to the deepest well at -58.87 kcal mol $^{-1}$; the connectivity of TSCh2 (pre-reactive region $\leftrightarrow$ POZCh2) was verified by intrinsic-reaction-coordinate analysis. A shallow van der Waals pre-complex precedes the Δ^3 saddle but does not control the rate.

3.2. Phenomenological rate coefficients

Table 2 summarizes the MESMER phenomenological rate coefficients for the three channels at 298.15 K and 760 Torr — the conditions that match the SAR reference point of Khan et al. (10). All three channels return well-defined, slow rate constants: $k_{\Delta^7} = 2.50 \times 10^{-21}$ and $k_{\Delta^1} = 1.45 \times 10^{-22}$ and $k_{\Delta^3} = 1.53 \times 10^{-23}$ cm ^{3} molecule $^{-1}$ s $^{-1}$. Across the temperature grid (250–400 K, 760 Torr) all three channels follow clean Arrhenius behavior; least-squares fits give (A in cm ^{3} molecule $^{-1}$ s $^{-1}$, activation energy in kcal mol $^{-1}$): Δ^7 , $A = 3.2 \times 10^{-14}$, $E_a = 9.7$; Δ^1 , $A = 2.6 \times 10^{-15}$, $E_a = 9.9$; Δ^3 , $A = 6.7 \times 10^{-16}$, $E_a = 10.4$. The effective activation energies exceed the ZPE-corrected electronic barriers (Table 1) because the bimolecular association entropy folds into the effective barrier, and the pre-exponential factors decrease in the order $\Delta^7 > \Delta^1 > \Delta^3$, mirroring the relative looseness of the three transition states and reinforcing the same channel ordering at every temperature studied.

The Channel 2 master-equation calculation, using the genuine cycloaddition transition state TSCh2 on the same RRKM/Eckart footing as the other two channels, returns $k_{\Delta^3} = 1.53 \times 10^{-23}$ cm ^{3} molecule $^{-1}$ s $^{-1}$ at 298.15 K and 760 Torr. This is the smallest of the three channel rate coefficients — about an order of magnitude below k_{Δ^1} and two orders below k_{Δ^7} — consistent with its being the

highest-barrier entrance. The internal Δ^3 double bond, despite being the more highly substituted olefin, is thus the slowest of the three ozone-attack sites in this molecule, not the fastest: the electron-withdrawing chlorine substituents and the conjugation of the backbone raise rather than lower its cycloaddition barrier. The associated POZCh2 well is the deepest of the three (-58.87 kcal mol $^{-1}$), but because the entrance is rate-limiting and the well is kinetically irreversible, the well depth does not enter the rate. A point worth emphasizing is that the three channels are not ordered by barrier height alone. The lowest barrier belongs to Δ^1 (+6.67 kcal mol $^{-1}$), yet Δ^7 (+7.02 kcal mol $^{-1}$) is the faster of the two by roughly an order of magnitude. The difference is entropic: the rovibrational partition function of the Δ^7 cycloaddition transition state is about five times larger than that of the tighter Δ^1 saddle ($Q_{vib}(298\text{ K}) \approx 4.3 \times 10^7$ versus 8.7×10^6), so the looser Δ^7 transition state more than compensates for its slightly higher barrier through a larger pre-exponential factor. The internal Δ^3 saddle is both the highest in energy and among the tightest ($Q_{vib} \approx 6.5 \times 10^6$), so the enthalpic and entropic factors reinforce one another to make it the slowest channel. Channel selectivity in this system is therefore governed by a balance of barrier height and transition-state entropy rather than by barrier height in isolation — a distinction that purely energetic or additive (SAR/MCM) arguments cannot

capture. The overall ordering of the three ozonolysis channels is accordingly $\Delta^7 > \Delta^1 > \Delta^3$, determined by the combination of entrance barrier and transition-state partition function: $k_{\Delta^7} = 2.50 \times$

$$10^{-21} > k_{\Delta^1} = 1.45 \times 10^{-22} > k_{\Delta^3} = 1.53 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Table 2: Phenomenological rate coefficients for the three ozonolysis channels of Compound 1 at 298.15 K and 760 Torr N₂ from single-channel MESMER master-equation analysis. All three entries proceed over genuine first-order cycloaddition transition states, treated identically with SimpleRRKM kinetics and Eckart tunneling.

Channel	Entry barrier (kcal mol ⁻¹)	k_{298} (cm ³ molecule ⁻¹ s ⁻¹)	Notes
Channel 1 (Δ^7 , terminal vinyl)	+7.02 (tight TS)	2.50×10^{-21}	Quantitative RRKM
Channel 2 (Δ^3 , internal)	+9.57 (tight TS)	1.53×10^{-23}	Quantitative RRKM
Channel 3 (Δ^1 , chloromethylene)	+6.67 (tight TS)	1.45×10^{-22}	Quantitative RRKM

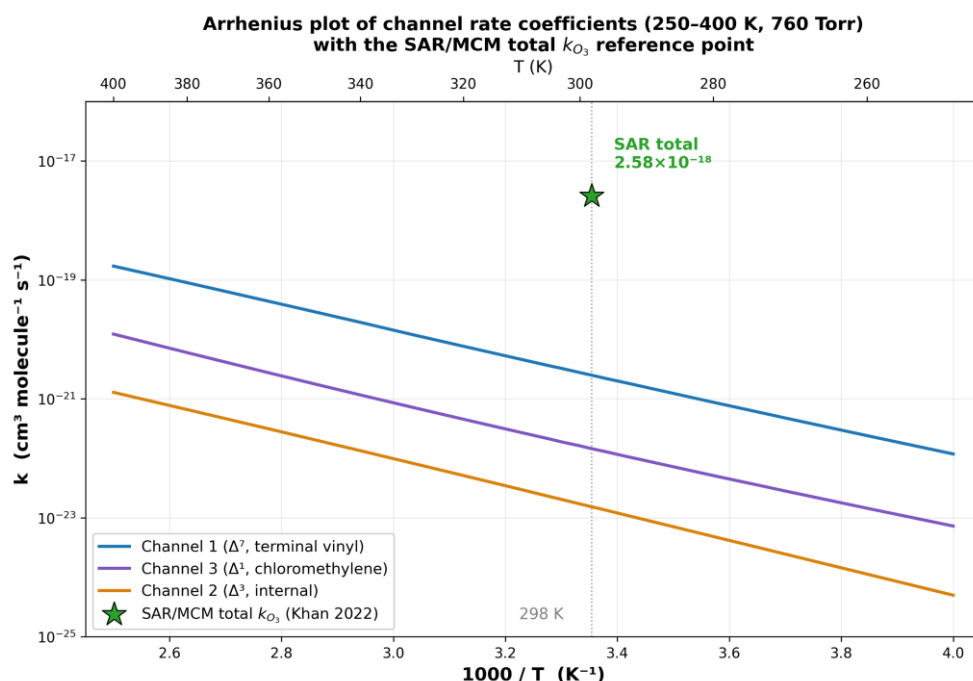


Figure 4: Arrhenius plot of the channel rate coefficients over 250–400 K at 760 Torr N₂, with the SAR/MCM total k_{O_3} reference of Khan et al. (10) shown as a single point at 298 K (green star). All three channels (Δ^7 , blue; Δ^1 , purple; Δ^3 , orange) follow clean Arrhenius behavior and lie well below the SAR total, in the order $\Delta^7 > \Delta^1 > \Delta^3$. The internal Δ^3 channel, with the highest entrance barrier (+9.57 kcal mol⁻¹) and the tightest transition state, is the lowest of the three curves ($k_{\Delta^3} = 1.53 \times 10^{-23}$ cm³ molecule⁻¹ s⁻¹ at 298 K).

3.3. Pressure dependence and collisional stabilization

The pressure dependence of the two barriered channels (Channels 1 and 3) follows the canonical falloff behavior for an association/dissociation system with a deep POZ well: the apparent overall bimolecular rate constant k_{overall} — the quantity plotted in Figure 5, which counts only those encounters that proceed through to dissociation products — decreases with increasing pressure as a growing fraction of the nascent primary ozonide is collisionally stabilized in the well rather than dissociating. For Channel 1, the prompt

(dissociating) fraction at 760 Torr is approximately 28%, with the remaining ~72% retained as the collisionally stabilized primary ozonide; the Channel 3 prompt fraction is of the same order. This prompt fraction should be read as an order-of-magnitude estimate rather than a precise value, because — unlike the entrance rate coefficients, which depend only on the cycloaddition barrier — the prompt-versus-stabilized partitioning is governed by the degree of chemical activation of the nascent ozonide and is therefore directly sensitive to the primary-ozonide well depth. Two sources of uncertainty bear on this depth: the conformational search above

shifts it by up to ~ 2 kcal mol $^{-1}$, and the M06-2X wells lie 11–13 kcal mol $^{-1}$ deeper than the DLPNO-CCSD(T) values (Section 3.3), so that the functional-derived uncertainty in the well depth alone could move the prompt fraction by a factor of order two. The qualitative conclusion — that the collisionally stabilized ozonide, not the free Criegee, is the dominant first-generation product at atmospheric pressure — is robust to this uncertainty. The dominant first-generation product of both barriered channels at atmospheric pressure is therefore the metastable stabilized primary

ozonide rather than the free Criegee intermediate, and the effective prompt Criegee yields from these channels are modest. Channel 2, with its tight cycloaddition entrance and the deepest POZ well (-58.87 kcal mol $^{-1}$), follows the same qualitative pressure-dependent pattern as the other two channels: a growing fraction of the chemically activated primary ozonide is collisionally stabilized as the pressure rises, so that the stabilized ozonide is again the dominant first-generation product at atmospheric pressure.

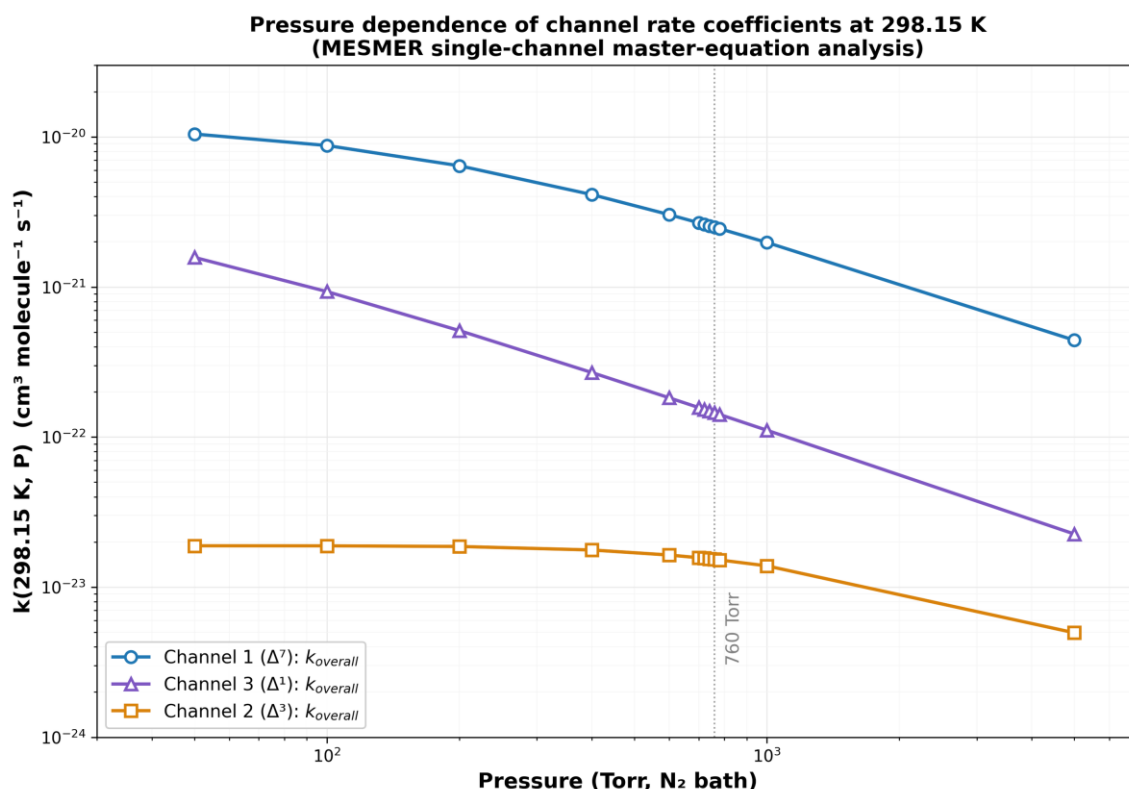


Figure 5: Pressure dependence of the overall phenomenological rate coefficients k_{overall} of the three ozonolysis channels at 298.15 K, from single-channel MESMER analysis. Channel 1 (Δ^7 , blue circles) shows the characteristic falloff of a barriered association/dissociation system: k_{overall} decreases with pressure as a growing fraction of the primary ozonide is collisionally stabilized in the well rather than dissociating to products. Channel 3 (Δ^1 , purple triangles) follows the same shape one order of magnitude lower. Channel 2 (Δ^3 , orange squares) shows the same falloff behavior a further order of magnitude below, consistent with its being the highest-barrier, slowest channel. The vertical dotted line marks the atmospheric reference pressure of 760 Torr.

3.4. Channel branching and comparison with the SAR baseline

Summing the three channel rate coefficients gives a total ozonolysis rate coefficient for Compound 1 of $k(\text{O}_3, \text{total}) = 2.66 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 760 Torr, partitioned approximately as $\Delta^7 \sim 94\%$, $\Delta^1 \sim 5\%$ and $\Delta^3 \sim 1\%$. These percentages are quoted to no better than their leading figure: the ~ 2 kcal mol $^{-1}$ spread between the DLPNO and M06-2X barriers (a factor of ~ 30 in rate at 298 K) and the factor 2–5 sensitivity to $\langle \Delta E \rangle$ down place an order-of-magnitude uncertainty on the absolute coefficients, so only the qualitative ordering and the dominance of Δ^7 are robust. The terminal Δ^7 vinyl is overwhelmingly the dominant ozone-attack site, the chloromethylene Δ^1 group is a minor channel,

and the internal Δ^3 double bond is a negligible contributor. This ordering is set by the combination of entrance barrier and transition-state entropy discussed in Section 3.2: the lowest absolute barrier (Δ^1) does not give the fastest channel, because the looser Δ^7 transition state carries the larger pre-exponential factor.

This branching agrees with the SAR/MCM partitioning of Khan et al. (10) — which assigns 93% of the flux to the terminal Δ^7 site and 7% to the internal Δ^3 site, with the chloromethylene Δ^1 site not separately treated — on the dominant site, but not on the minor chemistry. On the dominant channel, the two pictures coincide: both identify the terminal Δ^7 vinyl as the overwhelming ozone-attack

site, and the present explicit mechanism provides an independent, first-principles confirmation of that assignment. On the secondary chemistry, however, the present analysis is a reassignment rather than a confirmation: SAR/MCM treats the internal Δ^3 double bond as the secondary site (7%), whereas the explicit calculation finds Δ^3 to be the slowest of the three channels ($\sim 1\%$) and instead identifies the chloromethylene Δ^1 group — not considered by SAR — as the true secondary channel ($\sim 5\%$). The minor role SAR assigns to the internal double bond is therefore carried, in the explicit mechanism, by a different bond. The earlier suggestion — based on a single-coordinate approach scan — that the Δ^3 site might be barrierless and dominant is not supported once the correct synchronous reaction coordinate is used: the Δ^3 site is in fact the slowest of the three.

The two analyses differ in absolute magnitude rather than in branching. The total SAR ozonolysis estimate, $k(\text{O}_3, \text{SAR}) = 2.58 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, lies about three orders of magnitude greater than the present DLPNO+MESMER total. Even the dominant Δ^7 partial rate implied by SAR ($0.93 \times 2.58 \times 10^{-18} \approx 2.4 \times 10^{-18}$) exceeds the explicit $k(\Delta^7) = 2.50 \times 10^{-21}$ by three orders of magnitude. Two interpretations are possible, and in the absence of an experimental rate coefficient for Compound **1** they cannot be fully separated here. The first is that the SAR scheme, calibrated on sparsely substituted alkenes, overestimates cycloaddition rate coefficients for densely chlorinated, conjugated systems in which the electron-withdrawing substituents raise the cycloaddition barrier. The second is that the present workflow systematically overestimates the entrance barriers: the computed terminal-vinyl barrier ($+7.02 \text{ kcal mol}^{-1}$) exceeds the experimental ozonolysis barriers of simple terminal alkenes such as ethene and propene ($\sim 4\text{--}5 \text{ kcal mol}^{-1}$, with measured 298 K rate coefficients of order $10^{-18}\text{--}10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and the Δ^7 vinyl of Compound **1** lies several bonds from the chlorine substituents, so that a remote inductive effect alone producing a three-order-of-magnitude slowdown is a strong claim. To distinguish these possibilities, the identical workflow ($\omega\text{B97X-D3BJ/def2-TZVP}$ geometry and frequencies // DLPNO-CCSD(T)/def2-TZVPP single points) was applied to the ozonolysis of ethene, for which a well-established experimental rate coefficient and activation energy are available (Section 3.6). The workflow reproduces the experimental ethene ozonolysis barrier to within $0.4 \text{ kcal mol}^{-1}$ (computed 5.3 versus experimental $\sim 4.95 \text{ kcal mol}^{-1}$ (12,51)), demonstrating that it does not systematically overestimate cycloaddition barriers for simple alkenes. This benchmark therefore disfavors the second interpretation and supports the first: the three-order-of-magnitude SAR-theory gap reflects, at least in large part, an overestimation by the additive SAR scheme for this densely chlorinated, conjugated system rather than an error in the present barriers. Consistent with this, the computed Compound **1** terminal-vinyl barrier ($+7.02 \text{ kcal mol}^{-1}$) lies only $\sim 2 \text{ kcal mol}^{-1}$ above the benchmarked ethene value, a shift readily

attributable to the chlorine substitution and conjugation of the real substrate; the relative branching among the three channels, which depends on barrier differences rather than absolute values, is more robust still. The qualitative conclusion of Khan et al. (10) that OH-initiated oxidation dominates the atmospheric fate of Compound **1** is unaffected by this difference and remains a sound first approximation; the present work refines the ozonolysis branch and supplies the mechanistic detail — intermediates, energy partitioning and pressure dependence — that the SAR scheme cannot provide.

What is firmly established by the present analysis is the channel ordering $\Delta^7 > \Delta^1 > \Delta^3$ and its physical origin: channel selectivity in this densely chlorinated marine monoterpene is governed not by barrier height alone but by the interplay of barrier height and transition-state entropy. A channel-resolved re-examination of the SAR substituent factors for densely halogenated marine monoterpenes, anchored to explicit mechanistic calculations of the kind reported here, is therefore warranted. It should be emphasized that the ethene benchmark validates the computational methodology — confirming that the identical workflow does not systematically bias ozonolysis barriers — rather than serving as a direct chemical analog for this densely chlorinated, conjugated substrate. Throughout, the channel ordering ($\Delta^7 > \Delta^1 > \Delta^3$) is the robust, well-constrained outcome of this analysis, whereas the absolute rate coefficients carry a larger uncertainty, arising principally from the harmonic treatment of the low-frequency modes and the single-structure transition states.

3.5. Method cross-validation and energy-transfer sensitivity

To confirm that the channel ordering is not an artifact of the chosen density functional, the entrance barrier of every channel was recomputed at the M06-2X/def2-TZVP level on the common $\omega\text{B97X-D3BJ/def2-TZVP}$ geometry and zero-point basis used throughout. The two methods place the three entrance barriers in the same order and within $\sim 2 \text{ kcal mol}^{-1}$ of one another: Δ^7 $+7.02$ (DLPNO) versus $+5.01$ (M06-2X), Δ^1 $+6.67$ versus $+4.84$, and Δ^3 $+9.57$ versus $+7.39 \text{ kcal mol}^{-1}$. M06-2X lowers each barrier by a roughly constant $\approx 2 \text{ kcal mol}^{-1}$ but preserves the relative spacing, so that the internal Δ^3 saddle remains the highest and the two terminal-type saddles remain closely spaced at both levels. Because the kinetically decisive quantity is the entrance barrier, this agreement establishes that the channel ordering $\Delta^7 > \Delta^1 > \Delta^3$ is independent of the electronic-structure method. The post-barrier primary-ozonide well depths are more functional-sensitive (deeper by $\sim 11\text{--}13 \text{ kcal mol}^{-1}$ at M06-2X) but being kinetically irreversible, do not enter the rate coefficients.

The sensitivity to the collisional energy-transfer parameter was assessed by repeating each single-channel calculation for $\langle \Delta E \rangle_{\text{down}} = 150, 225$ and 300 cm^{-1} (extended to 500 cm^{-1} for Channel 1;

Table 3). A larger $\langle \Delta E \rangle_{\text{down}}$ diverts a greater fraction of the chemically activated primary ozonide into collisional stabilization, so the prompt-bimolecular coefficient decreases monotonically with $\langle \Delta E \rangle_{\text{down}}$. For the internal Δ^3 channel the prompt-bimolecular coefficient varies smoothly from 1.78×10^{-23} (150 cm^{-1}) through 1.53×10^{-23} (225 cm^{-1}) to $1.29 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 cm^{-1}), a total spread of only $\sim 1.4\times$; the two barriered channels show comparably bounded

variation (a factor of about 2.9 for Δ^1 across $150\text{--}300 \text{ cm}^{-1}$ and 4.6 for Δ^7 across $150\text{--}500 \text{ cm}^{-1}$). The channel ordering $\Delta^7 > \Delta^1 > \Delta^3$ is unchanged across the entire range. The pressure-dependent partitioning between prompt Criegee formation and stabilized primary ozonide therefore carries a bounded, explicitly quantified uncertainty, while the qualitative kinetic picture is insensitive to this parameter.

Table 3: Method cross-validation and energy-transfer sensitivity. Column 2 gives the prompt-bimolecular DLPNO-CCSD(T) rate coefficient ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at $\langle \Delta E \rangle_{\text{down}} = 225 \text{ cm}^{-1}$; column 3 gives the M06-2X/def2-TZVP entrance barrier (kcal mol^{-1} , ZPE-corrected) for comparison with the corresponding DLPNO+ZPE barriers (Table 1); columns 4–5 give the DLPNO-CCSD(T) rate coefficients at $\langle \Delta E \rangle_{\text{down}} = 150$ and 300 cm^{-1} . All three channels are treated identically, each over a genuine first-order cycloaddition transition state. The two functionals place the three entrance barriers in the same order ($\Delta^1 < \Delta^7 < \Delta^3$), confirming that the channel ordering is independent of the electronic-structure method.

Channel	DLPNO k (225)	M06-2X barrier	DLPNO k (150)	DLPNO k (300)
Δ^7	2.50×10^{-21}	+5.01	4.21×10^{-21}	1.72×10^{-21}
Δ^1	1.45×10^{-22}	+4.84	2.76×10^{-22}	9.49×10^{-23}
Δ^3	1.53×10^{-23}	+7.39	1.78×10^{-23}	1.29×10^{-23}

3.6. Limitations and outlook

Several methodological caveats should be stated explicitly. First, all three entrance transition states, including the internal Δ^3 saddle TSCh2 identified here via the synchronous two-bond coordinate, were optimized from single, chemically reasonable structures, and the low-frequency modes were treated within the harmonic-oscillator approximation; a systematic multistructural and torsional treatment of the conformationally flexible cycloaddition transition states would refine the entropic prefactors, and hence the absolute value of k_{Δ^3} . This refinement is expected to shift the absolute rate coefficients modestly but not to alter the channel ordering, which is set by the well-separated entrance barriers. Second, the combined three-channel master-equation analysis that was attempted at an earlier stage proved numerically ill-conditioned, with the Bartis–Widom eigenvalue spectrum failing to separate cleanly; the single-channel analysis adopted here yields well-conditioned phenomenological rate coefficients for each channel taken in isolation but does not account for any inter-channel coupling through, for example, isomerization between primary ozonides. For the present chemistry, in which the three POZ wells lie at comparable depths and are separated by very high effective barriers (the retro-cycloaddition transition states), this coupling is expected to be negligible, but a rigorous demonstration would require a tractable multi-well treatment. Third, the cross-validation against M06-2X has been carried out at the level of the entrance barriers of all three channels; it confirms that the rate-determining barriers are robust to the functional choice both in magnitude (agreement within $\sim 2 \text{ kcal mol}^{-1}$) and, crucially, in their ordering ($\Delta^1 < \Delta^7 < \Delta^3$), while the (non-rate-determining) primary-ozonide well depths are systematically deeper at M06-2X and are the more functionally-sensitive quantity. Fourth, no direct experimental rate coefficient is available for Compound 1; the present results are validated

against internal consistency (M06-2X barrier cross-validation, IRC connectivity of all transition states including TSCh2, T_1 diagnostics) and against literature barrier and well-depth ranges for related alkene- O_3 systems (35–38). A benchmark of the workflow against a system with a known experimental k_{O_3} provides an external anchor: because the central comparison of this work is with the SAR estimate, and the two diverge by three orders of magnitude (Section 3.4), establishing whether the present workflow reproduces a measured ozonolysis rate coefficient to within a small factor — for a simple alkene such as ethene or propene, or a simple chloroalkene, run through the identical $\omega\text{B97X-D3BJ} \rightarrow \text{DLPNO-CCSD(T)} \rightarrow \text{MESMER}$ pipeline with the same $\langle \Delta E \rangle_{\text{down}}$ and grid — was required to decide whether the SAR-theory gap reflects SAR overestimation or a systematic offset in the computed barriers. This anchor was computed explicitly: the ethene + O_3 cycloaddition transition state was located as a genuine first-order saddle point (single imaginary mode at $572i \text{ cm}^{-1}$, symmetric $\text{C}\cdots\text{O}$ forming distances of $2.22 \text{ \AA}$, T_1 diagnostic 0.018), giving a ZPE-corrected barrier of $5.3 \text{ kcal mol}^{-1}$ in close agreement with the experimental Arrhenius activation energy for ethene ozonolysis of $\sim 4.95 \text{ kcal mol}^{-1}$ (12,51) (a difference of only $0.4 \text{ kcal mol}^{-1}$). This establishes that the present workflow does not systematically overestimate ozonolysis barriers for simple alkenes, so the large SAR-theory discrepancy for Compound 1 is most plausibly attributed to overestimation by the additive SAR scheme for this densely chlorinated, conjugated substrate rather than to an offset in the computed barriers; the computed terminal-vinyl barrier ($+7.02 \text{ kcal mol}^{-1}$) lies only about 2 kcal mol^{-1} above the benchmarked ethene value, consistent with the additional chlorine substitution and conjugation of the real substrate. Fifth, the conformational space of the flexible stationary points was examined explicitly. A systematic conformer-rotamer ensemble search

(CREST (49), GFN-FF (50)) was carried out for the three primary ozonides, generating 30, 40 and 82 conformers for the Δ^7 , Δ^3 and Δ^1 ozonides, respectively, with the trioxolane ring preserved throughout. Re-optimization of the lowest-energy conformer of each ozonide at the ω B97X-D3BJ/def2-TZVP level changed the primary-ozonide well depths by -1.9 kcal mol $^{-1}$ (Δ^7) and -0.8 kcal mol $^{-1}$ (Δ^1), while for the Δ^3 ozonide the original structure was confirmed as the lowest conformer (the lowest CREST candidate lying 6.4 kcal mol $^{-1}$ higher after re-optimization). These shifts (≤ 2 kcal mol $^{-1}$) are reported at the ω B97X-D3BJ geometry level and would be altered only marginally by DLPNO-CCSD(T) single points; crucially, they affect only the absolute primary-ozonide well depths and therefore propagate solely to the prompt-versus-stabilized Criegee partitioning, not to the entrance-channel rate coefficients or the $\Delta^7 > \Delta^1 > \Delta^3$ ordering, which are governed by the cycloaddition transition states that lie kinetically upstream of the ozonide wells. Sixth, the low-frequency torsional modes were treated within the harmonic-oscillator approximation rather than as hindered internal rotors; an explicit hindered-rotor treatment would refine the partition functions, and hence the entropic component of the rate coefficients, although its effect on the relative ordering of the channels is expected to be small. Seventh, the single-exponential-down collisional energy-transfer parameter ($\langle \Delta E \rangle_{\text{down}} = 225$ cm $^{-1}$ in N $_2$) was taken from the established literature range, and its influence was assessed explicitly through the sensitivity scan reported in Section 3.5: across $\langle \Delta E \rangle_{\text{down}} = 150\text{--}300$ cm $^{-1}$ (extended to 500 cm $^{-1}$ for Channel 1) the qualitative falloff behavior and the channel ordering are unchanged, while the absolute prompt-bimolecular coefficients vary by a factor of roughly two to five; this parameter therefore contributes a bounded, quantified uncertainty to the pressure-dependent branching rather than an open-ended one.

Three follow-up directions are identified by the workflow developed here. (i) Multistructural and hindered-rotor refinement of the three cycloaddition transition states — and, where the entrance is loose, a variable-reaction-coordinate or variational treatment (45–47) — to convert the present harmonic rate coefficients into fully converged values and tighten the absolute total ozonolysis rate of Compound **1**. (ii) Extension of the same pipeline to the OH-initiated oxidation of Compound **1** — the dominant atmospheric loss pathway — and to the remaining Plocamium-derived monoterpenes. (iii) Experimental detection of the stabilized primary ozonides identified here as kinetically retained at atmospheric pressure (Section 3.3), which would be a direct fingerprint of the chemistry described in the present work and a natural target for forthcoming flow-tube FT-CIMS experiments.

4. CONCLUSION

A cost-free computational workflow — combining the open-source packages Avogadro 2 and Open

Babel (molecular construction) and MESMER 7.1 (master-equation kinetics) with ORCA 6.1 (free of charge for academic use) for ω B97X-D3BJ/def2-TZVP optimization and DLPNO-CCSD(T)/def2-TZVPP single-point refinement, together with an independent M06-2X/def2-TZVP cross-validation — has been applied to the three ozonolysis channels of Compound **1** of the marine macroalgal halogenated-monoterpene inventory of Khan et al. (10), 5,6-dichloro-2-chloromethylene-6-methyl-octa-3,7-dienal (C $_{10}$ H $_{11}$ Cl $_3$ O).

All three channels proceed over tight, first-order cycloaddition transition states to deep primary ozonides. The terminal Δ^7 vinyl (Channel 1) and chloromethylene Δ^1 (Channel 3) channels pass over saddles at +7.02 and +6.67 kcal mol $^{-1}$ to wells at -53.36 and -54.68 kcal mol $^{-1}$, with phenomenological rate coefficients of 2.50×10^{-21} and 1.45×10^{-22} cm ^{3} molecule $^{-1}$ s $^{-1}$ respectively at 298 K and 760 Torr. Both exhibit substantial pressure-dependent collisional stabilization of the primary ozonide, so that the stabilized ozonide — rather than the free Criegee intermediate — is the dominant first-generation product at atmospheric pressure (prompt Criegee yields $\sim 28\%$). The internal Δ^3 channel (Channel 2), initially suspected to be barrierless from a single-coordinate approach scan, was shown by a synchronous two-bond scan, transition-state optimization and IRC analysis to proceed over a genuine concerted cycloaddition saddle (one imaginary mode, -310 cm $^{-1}$) at +9.57 kcal mol $^{-1}$ — the highest of the three entrance barriers — giving the smallest rate coefficient, $k_{\Delta^3} = 1.53 \times 10^{-23}$ cm ^{3} molecule $^{-1}$ s $^{-1}$, making the internal double bond the slowest rather than the fastest of the three ozone-attack sites.

The resulting branching — $\Delta^7 \sim 94\%$, $\Delta^1 \sim 5\%$, $\Delta^3 \sim 1\%$ — confirms the SAR/MCM picture of Khan et al. (10) on the dominant site (Δ^7) but reassigns the minor chemistry: SAR treats the internal Δ^3 double bond as the secondary site, whereas the explicit mechanism finds Δ^3 to be the slowest channel and the chloromethylene Δ^1 group, not considered by SAR, to be the true secondary channel. The channel ordering is governed not by barrier height alone but by the interplay of entrance barrier and transition-state entropy: although Δ^1 has the lowest barrier, the looser Δ^7 transition state — with a rovibrational partition function some five times larger — makes Δ^7 the dominant channel, while the internal Δ^3 saddle, both the highest in energy and the tightest, is the slowest. The present DLPNO+MESMER total ozonolysis rate lies about three orders of magnitude below the SAR estimate. Benchmarking the identical workflow against ethene ozonolysis — which reproduces the experimental barrier to within 0.4 kcal mol $^{-1}$ — shows that this gap does not arise from a systematic overestimation of barriers by the workflow, and is therefore most plausibly attributed to the known tendency of additive SAR factors to overestimate cycloaddition rates for densely chlorinated, conjugated systems; a channel-resolved re-examination of the SAR substituent factors for halogenated marine monoterpenes, anchored to explicit mechanistic calculations and to

experimentally constrained benchmarks, is therefore warranted.

The methodological contribution of the present work is the demonstration that a complete three-channel mechanistic-kinetic workflow for atmospheric reactions — capable of resolving each elementary step from pre-reactive complex through Criegee intermediate formation, and of distinguishing channel selectivity that arises from transition-state entropy rather than barrier height alone — can be implemented on a single workstation at zero software cost. The analysis also illustrates a methodological caution: a relaxed single-bond approach scan can falsely suggest a barrierless entry for a concerted cycloaddition, and the synchronous two-bond coordinate is required to expose the true saddle point. The workflow is now ready for application to the OH-initiated oxidation of Compound **1** and for extension to the remaining Plocamium-derived halogenated monoterpenes; its predictions are designed to be tested against forthcoming flow-tube FT-CIMS measurements aimed at quantifying the contribution of marine halogenated-monoterpene Criegee chemistry to secondary organic aerosol and cloud condensation nuclei formation.

SUPPORTING INFORMATION

The Supporting Information contains: optimized Cartesian coordinates (Å) of all stationary points of the three channels (reactant, the cycloaddition transition states TS_{Ch1} and TS_{Ch3}, the internal-cycloaddition transition state TS_{Ch2}, the three primary ozonides POZ_{Ch1}, POZ_{Ch2}, POZ_{Ch3}, the three retro-cycloaddition transition states, and the six product fragments) at the ωB97X-D3BJ/def2-TZVP level; the corresponding absolute electronic energies, zero-point vibrational energies, DLPNO-CCSD(T)/def2-TZVPP single-point energies and T₁ diagnostics; the full harmonic vibrational frequencies (including the single imaginary frequency of each transition state, −296.36, −323.12 and −310.02 cm^{−1} for TS_{Ch1}, TS_{Ch3} and TS_{Ch2}, respectively); the M06-2X/def2-TZVP entrance-barrier values for all three channels; the complete MESMER 7.1 input XML files for the three single-channel calculations; and the tabulated k(T, P) grids.

5. CONFLICT OF INTEREST

The author declares no conflict of interest.

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