

FULL PAPER

A computational investigation of the sulphuric acid-catalysed 1,4-hydrogen transfer in higher Criegee intermediates

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Abstract

Criegee intermediates (CIs) are formed during the ozonolysis of unsaturated hydrocarbons in the troposphere. The fate of CIs is of critical importance to tropospheric oxidation chemistry, particularly in the context of radical and secondary organic aerosol formation. Using the high-level ab initio G4(MP2) method, we investigate the 1,4 hydrogen shift reaction in CIs formed from ozonolysis of two common biogenic hydrocarbons: isoprene and α -pinene. We consider the uncatalysed reaction, as well as the reaction catalysed by a water molecule and by sulphuric acid. We show that sulphuric acid is a very effective catalyst, leading to a barrierless tautomerization relative to the free reactants and to very low reaction barrier heights relative to the reactant complexes. In particular, we obtain reaction barrier heights of $\Delta H_{298}^{\ddagger} = 24.5$ (isoprene CI) and 8.4 (α -pinene CI) kJ mol⁻¹ relative to the reactant complexes. Given the reaction of OH radicals with SO₂ in the troposphere can ultimately yield sulphuric acid, these findings may have significant consequences for current atmospheric chemical models for regions of high sulphur concentrations.

KEYWORDS

CCSD(T), Criegee intermediates, G4(MP2), inorganic acid catalysis, water catalysis

1 | INTRODUCTION

The oxidation of olefin bonds by ozone (termed ozonolysis) is a major removal process for unsaturated hydrocarbons in the troposphere.^[1-4] A critical component of the reaction mechanism is the Criegee intermediate (CI), which retains a significant portion of the nascent energy from ozonolysis and can undergo either unimolecular decomposition or collisional stabilization with the bath gas, after which bimolecular reaction with trace atmospheric species (e.g., H₂O, NO, NO₂, SO₂, organic acids, and aldehydes) becomes important. Mechanistically, CIs show considerable variation in the literature, with size and functionalization dictating branching ratios of the various excited and stabilization channels.^[5-7] Knowledge of these pathways is important, as the fate of CIs has an important impact on global tropospheric chemistry, directly influencing free radical and aerosol budgets.^[2,3,8]

Despite extensive experimental work on the ozonolysis mechanism,^[9-12] considerable uncertainty remains due to the extremely short lifetimes of CI species. CIs have been experimentally detected from the gas-phase ozonolysis of alkenes,^[13,14] however, much of our understanding of the ozonolysis mechanism comes indirectly from measurements of stable products interfaced with computational studies for potential energy surface mapping. Computational studies show that for excited CIs existing in the *syn*-conformation, that is with the carbonyl oxide moiety orientated toward an adjacent hydrogen-containing group, a 1,4-hydrogen transfer to an excited vinylhydroperoxide (VHP) is typically the preferred unimolecular decomposition route.^[4,6] The mechanism leading to VHP production from the ozonolysis reaction is shown in Figure 1. In addition, geometries of Criegee intermediates show that there is a partial double bond between the carbon and oxygen, indicating that these structures can be described to some extent as closed shell, or charge separated zwitterions rather than biradical species.^[15,16]

Experiments have shown that the VHP may be subject to considerable stabilization under atmospheric conditions,^[17] however, for the most part, decomposition into a vinoxy radical and hydroxyl radical is assumed. Termed the hydroperoxide channel, the pathway represents an important source of nonphotolytic OH in the troposphere. This is important, especially at night, as the OH radical plays a central role in the oxidation chemistry of the troposphere. Reaction with the hydroxyl radical is the major removal process for most organics in the troposphere, while the reaction of OH

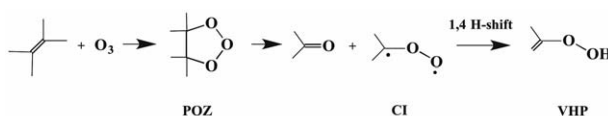


FIGURE 1 Formation of vinylhydroperoxides (VHPs) via ozonolysis followed by a 1,4 H-shift. Attack of ozone on the C=C double bond leads to a primary ozonide (POZ), which rapidly decomposes, yielding Criegee intermediates (CIs), then a 1,4 H-shift from the *syn* methyl group leads to the formation of VHPs

with SO_2 yields sulphuric acid, impacting aerosol formation and consequently the Earth's climate.^[18] The study of channels influencing OH production from CIs is, therefore, of considerable interest.

Computational investigations into the hydroperoxide channel have tended to focus on simple CIs. Long et al.^[19] used the high-level composite method W3X-L^[20] to explore the barrier height for the uncatalysed 1,4 H-shift isomerization in CH_3CHOO . W3X-L theory is a variant of the original W3-F12 theory (see also Ref. 21 for a recent review),^[22] which approximates the CCSDT(Q)/CBS electronic energy (i.e., coupled cluster with single, double, triple, and quasiperturbative quadruple excitations at the infinite basis-set limit) and includes core-valence, relativistic, and zero-point vibrational energy corrections. Yin et al.^[6] investigated the substituent effect on the barrier height of the 1,4 H-shift reaction in simple CIs at the QCISD(T)/CBS level of theory (quadratic configuration interaction with single, double, and perturbative triple excitations at the complete basis set limit). They showed VHP formation to dominate for saturated *syn*-conformers and dioxiranes for unsaturated CIs. Kumar et al.^[23] showed a 1,4 H-shift in CH_3CHOO to be catalysed by both water and small organic acids at the CCSD(T)/aug-cc-pVTZ level of theory (where CCSD(T) indicates coupled cluster theory with singles, doubles, and quasiperturbative triple excitations). Based on the ability of sulphuric acid to facilitate hydrogen transfers in CH_3O radicals,^[24] $\text{SO}_3\text{—H}_2\text{O}$ systems,^[25] and in other systems,^[26–29] Kumar et al.^[23] suggested that sulphuric acid could potentially catalyse 1,4-hydrogen transfers in CIs, however, the reaction mechanism for sulphuric acid catalysis has not been reported. Sulphuric acid catalysis of 1,4-H transfers in CIs is particularly important when considering (i) the ubiquity of H_2SO_4 in the troposphere, (ii) OH produced from CI decomposition can react with SO_2 to yield sulphuric acid, (iii) direct reaction of stabilized CI with SO_2 can produce sulphuric acid in the gas phase,^[30–33] and (iv) sulphuric acid vapour is almost always involved in atmospheric new particle formation.^[18,34–36]

Biogenic substances dominate the global emission budget of organic vapors into the atmosphere.^[37,38] The most commonly emitted biogenic into the troposphere is isoprene (C_5H_8 , Figure 2A), the simplest terpenoid, whose global emission is estimated at $5.4 \times 10^{14} \text{ g year}^{-1}$.^[38] However, α -pinene ($\text{C}_{10}\text{H}_{16}$, Figure 2B), the most commonly emitted monoterpene, has also received considerable interest owing to its large emission rate ($6.6 \times 10^{13} \text{ g year}^{-1}$),^[38] high tropospheric reactivity and propensity of oxidation products to form secondary organic aerosol.^[11,39–41] Indeed, studies have shown stabilized CIs from both isoprene and α -pinene actively participate in secondary organic aerosol formation,^[42–44] while an autoxidation mechanism stemming from a 1,4-H transfer in the ozonolysis mechanism of α -pinene has been used to explain particle nucleation events in forested regions.^[45–47]

Due to water being the dominant trace species in the troposphere, its potential catalytic influence on the bimolecular chemistry of CIs has been examined numerous times in the literature (for a recent review see Vereecken et al.^[4] and references therein). The reaction of CI with water is predicted to predominantly form hydroxyl-alkylhydroperoxides, however, research has shown that a water molecule can catalyse a H-migration to form a VHP in terpene-derived CI.^[23,48,49]

In the present work, we use the high-level *ab initio* G4(MP2) procedure^[50] to study the sulphuric acid-catalysed unimolecular 1,4 H-shift reactions in CIs. To make comparisons with the previous theoretical investigations, the uncatalysed and water-catalysed reactions are also considered using the same theoretical description. We begin by exploring the potential energy surfaces (PESs) of the simple methyl CI (CH_3CHOO), before translating the mechanism to more complex CIs derived from isoprene and α -pinene ozonolysis. We find that a sulphuric acid catalyst affords a barrierless reaction pathway for the 1,4-H tautomerization in CI, suggesting the pathway to be competitive with unimolecular decay and reaction with water as key CI loss processes in regions with high sulphuric acid concentrations.

2 | COMPUTATIONAL DETAILS

The high-level, *ab initio*, composite G4(MP2) theory^[50] was used to explore the enthalpic PES at 298 K (ΔH_{298}) for the uncatalysed and catalysed reactions of 1,4 H-shift in all CIs. The G4(MP2) composite protocol is an efficient composite procedure for approximating the CCSD(T) energy in

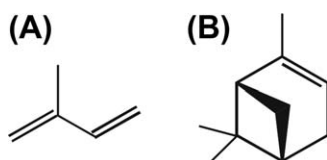


FIGURE 2 Structures of the (A) isoprene and (B) α -pinene molecules

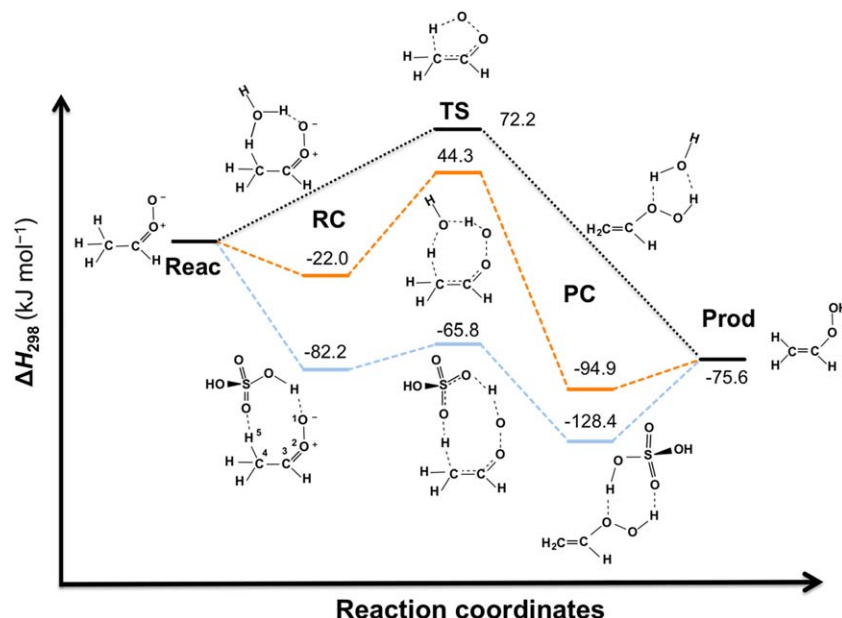


FIGURE 3 Reaction profile (G4(MP2), ΔH_{298} , kJ mol^{-1}) for the uncatalysed (black line), water-catalysed (orange line), and sulphuric acid-catalysed (blue line) reactions for 1,4 H-shift in methyl CI along with a schematic representation of species located along the reaction profile. For a picture of the optimized TSs see Figure S1 of the Supporting Information

conjunction with a large triple- ζ -quality basis set.^[51] This protocol is widely used for the calculation of thermochemical and kinetic properties (for recent reviews of the Gaussian- n methods and other composite methods see Refs. [21] and [51]). G4(MP2) theory has been found to produce thermochemical 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.^[50,52] It has also been found that G4(MP2) shows a similarly good performance for reaction barrier heights.^[53–56] Finally, we note that the main text primarily looks at ΔH_{298} values, however, similar trends in the reactivity and catalytic activity are observed on the Gibbs free energy (ΔG_{298}) reaction profiles (for further details see Figures S2–S4 of the Supporting Information).

The Gaussian 09 suite of programs was used for all the ab initio and DFT calculations.^[57] 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. Harmonic vibrational analyses have been performed at the same level of theory 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). The connectivity of the local minima and first-order saddle points was confirmed by performing intrinsic reaction coordinate calculations.^[58,59]

3 | RESULTS AND DISCUSSION

3.1 | Uncatalysed 1,4 H-shift reaction of methyl Criegee intermediate (CH_3CHOO)

In the absence of a catalyst, the 1,4 hydrogen transfer in methyl CI occurs through a concerted mechanism involving a 5-membered cyclic transition structure. For *syn*- CH_3CHOO a reaction barrier of $\Delta H_{298}^\ddagger = 72.2 \text{ kJ mol}^{-1}$ is obtained at the G4(MP2) level (Figure 3; the reaction barrier at 0 K is $\Delta H_0^\ddagger = 74.4 \text{ kJ mol}^{-1}$). This result is in good agreement with previous computational investigations. For example, Kuwata et al.^[60] obtained a reaction barrier height of $\Delta H_0^\ddagger = 75.3 \text{ kJ mol}^{-1}$ using the CBS-QB3 composite method.^[61] Similarly, Fang et al.^[62] investigated this isomerization at a comparable level of theory and arrived at a barrier of $\Delta H_0^\ddagger = 71.5 \text{ kJ mol}^{-1}$. Kidwell et al.^[63] obtained a slightly lower reaction barrier of $\Delta H_0^\ddagger = 67.8 \text{ kJ mol}^{-1}$ at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Yin and Takahashi calculated a barrier of $\Delta H_0^\ddagger = 70.3 \text{ kJ mol}^{-1}$ at the QCISD(T)/CBS level of theory (including a core-valence correction).^[6] Long et al. calculated a barrier of $\Delta H_0^\ddagger = 71.2 \text{ kJ mol}^{-1}$ at the CCSDT(Q)/CBS level of theory (using the high-level W3X-L composite method).^[19] This benchmark value is in reasonable agreement with the above ΔH_0^\ddagger values, which were calculated using lower levels of theory. In particular, the differences do not exceed the threshold of chemical accuracy (arbitrarily defined as $1 \text{ kcal mol}^{-1} \approx 4.2 \text{ kJ mol}^{-1}$). Finally, we note that Kumar et al.^[23] calculated a reaction barrier height of $\Delta G_{298}^\ddagger = 69.9 \text{ kJ mol}^{-1}$ on the Gibbs free-energy surface at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory. For additional discussions of the uncatalysed reaction see also Refs. [2] and [64]. The *anti*-conformer of methyl CI has no accessible 1,4-H transfer channel available, and so is not considered in this work.

3.2 | 1,4 H-shift reaction of methyl Criegee intermediate (CH_3CHOO) catalysed by water and sulphuric acid

Figure 3 shows a schematic representation of the PES at 298 K relative to the free reactants for the water-catalysed and sulphuric acid-catalysed pathways. We begin with exploring the PES for the 1,4 H-shift reaction of CH_3CHOO catalysed by a water molecule. In the reactant complex (RC),

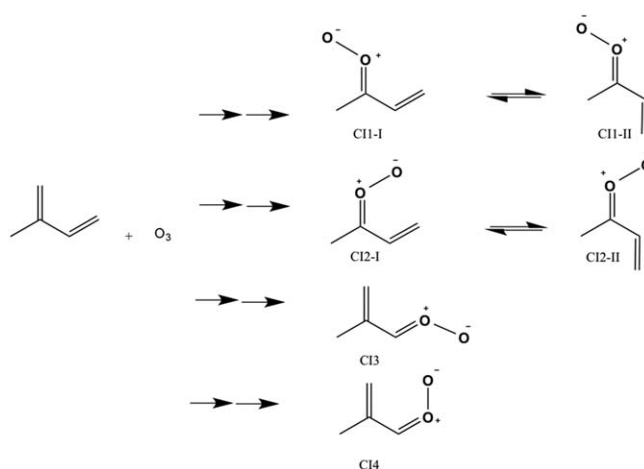


FIGURE 4 Species involved in the pathway for 1,4 H-shifts of isoprene Criegee intermediates leading to vinylhydroperoxides (VHPs)

the water molecule is hydrogen bonded to the CI by one hydrogen bond ($\text{HOH}\cdots\text{OO}$, 1.842 Å). As a result the RC in the water-catalysed reaction is more stable than the free reactants by 22.0 kJ mol^{-1} . The water catalyst reduces the reaction barrier for the hydrogen shift reaction by converting the uncatalysed five-membered ring TS into a 7-membered ring TS. The reaction barrier relative to the free reactants is $\Delta H_{298}^{\ddagger} = 44.3 \text{ kJ mol}^{-1}$, however, relative to the RC the reaction barrier is $\Delta H_{298}^{\ddagger} = 66.3 \text{ kJ mol}^{-1}$. That is, the reaction barrier for the water-catalysed pathway is lower by merely 5.9 kJ mol^{-1} relative to the reaction barrier of the uncatalysed pathway. This result is consistent with the previous investigation carried out with the W3X-L composite method,^[19] which found that a water molecule reduces the reaction barrier height of the 1,4-H shift by 2.3 kJ mol^{-1} . The transition structure (TS) leads to the formation of the product complex (PC), which lies 19.3 kJ mol^{-1} below the energy of the free products (methyl CI and water). This is attributed to the hydrogen bond between the hydrogen of vinylhydroperoxide (Prod) and the oxygen of the water catalyst ($\text{H}_2\text{O}\cdots\text{HOO}$, 1.838 Å).

With the assistance of a sulphuric acid molecule, the 1,4-H isomerization in CH_3CHOO becomes a barrierless process with respect to the free reactants (Figure 3). The RC formed between CI and sulphuric acid lies as much as 82.2 kJ mol^{-1} below the energy of the free reactants. In the RC, the sulphuric acid is hydrogen bonded with the CI with a fairly short $\text{SOH}\cdots\text{OO}$ hydrogen bond of 1.452 Å, indicating a strong H-bonding interaction (for comparison, the length of the $\text{SOH}\cdots\text{O}=\text{C}$ hydrogen bond between sulphuric acid and acetaldehyde is 1.638 Å).^[27] The RC also exhibits a short electrostatic interaction of 2.364 Å between the $\text{S}=\text{O}$ bond in H_2SO_4 and the β -hydrogen atom in CI.^[65] This is demonstrated by the following atomic polar tensor^[66,67] (APT) charges -0.292 (C^4), $+0.326$ (H^5), and -0.785 (O^6) (see Figure 3 for the atom numbers). For comparison the APT charges for the free methyl CI are $+0.006$ and $+0.009$ on C^4 and H^5 , respectively.

In the sulphuric acid-catalysed pathway, formation of the vinylhydroperoxide (Prod) proceeds through an efficient double hydrogen shift reaction involving a hydrogen-bonded TS complex. The reaction thus occurs through a 9-membered cyclic TS. A low reaction barrier height of merely 16.4 kJ mol^{-1} is obtained with respect to the RC, representing a submerged barrier relative to the free reactants (namely, the TS lies 65.8 kJ mol^{-1} below the free reactants). Thus sulphuric acid is a much better catalyst than H_2O , for which the TS lies 44.3 kJ mol^{-1} above the free reactants. The significant reduction in the barrier height for the hydrogen transfer is partly attributed to the reduced ring strain in the sulphuric acid-catalysed TS.^[23,27] Further inspection of the H_2SO_4 -catalysed TS shows that the distance of the bond between C^4 and H^5 (see Figure 3), which is being dissociated in the TS, decreases in the order uncatalysed TS (1.332 Å) > water-catalysed TS (1.291 Å) \gg H_2SO_4 -catalysed TS (1.035 Å). This trend indicates that the TS becomes earlier (less distorted) and, therefore, lower in energy in the same order. Finally, we note that the complex formed between the product and the sulphuric acid catalyst involves two intermolecular hydrogen bonds and is associated with relatively large complexation energy of 52.8 kJ mol^{-1} , relative to the free products. We note that the H-bond distances in PC are 1.765 Å (for the $\text{S}=\text{O}\cdots\text{HOO}$ bond) and 1.909 Å (for the $\text{S}=\text{OH}\cdots\text{O}(\text{OH})\text{CH}=\text{CH}_2$ bond) (see Figure 3).

3.3 | 1,4 H-shift reactions of isoprene Criegee intermediate

The ozonolysis of isoprene leads to four possible Criegee intermediates, two from addition to either double bond. These are shown in Figure 4 and include *syn* (CI2, CI4) and *anti* (CI1, CI3) CI conformers with respect to the adjacent vinyl group for each CI. In addition, CI1 and CI2 exist in two distinct conformations (CI1-I and CI1-II, CI2-I and CI2-II), arising from a partial π -bond character of the central C—C bond in CI. Of these species, only CI1 has a β -hydrogen available for abstraction on the neighboring methyl group. We note that abstraction of the vinyl hydrogen in CI2-II would yield a highly energetic allene, which previous works have shown to be uncompetitive.^[64] Therefore, the following discussion will focus on the CI1-I and CI1-II intermediates (Figure 4).

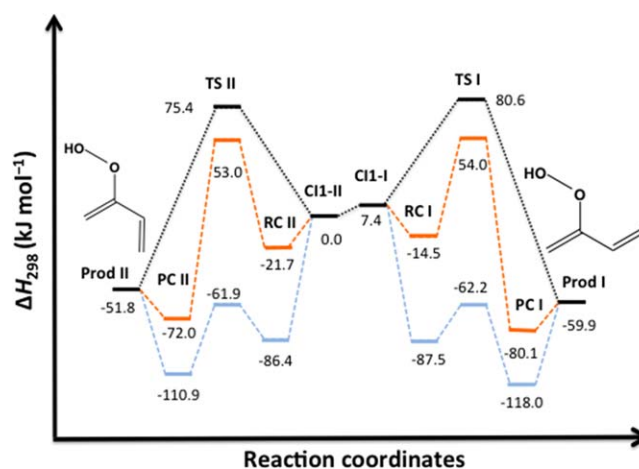


FIGURE 5 Reaction profiles (G4(MP2), ΔH_{298} , kJ mol^{-1}) for the uncatalysed (black line), water-catalysed (orange line), and sulphuric acid-catalysed (blue line) reactions for the 1,4 H-shifts of isoprene CI

At the G4(MP2) level of theory the **CI1-II** conformer is more stable than the **CI1-I** conformer by 7.4 kJ mol^{-1} . Inspection of the APT charges on the carbonyl carbon and oxygen reveals that both atoms are positively charged in both conformers. In particular, in **CI1-I** we obtain APT charges of 0.344 (C) and 0.155 (O) a.u. and in **CI1-II** we obtain charges of 0.287 (C) and 0.093 (O) a.u. Thus, the greater stability of **CI1-II** may be partially attributed to the smaller electrostatic repulsion between these two atoms.

The PES for the uncatalysed, water-catalysed, and sulphuric acid-catalysed 1,4 H-shift isomerizations in isoprene (**CI1-I** and **CI1-II**) are shown in Figure 5. All energies in Figure 5 are given with respect to the most stable form of the reactant (**CI1-II**). For the uncatalysed process we obtain reaction barriers of 80.6 and 75.4 kJ mol^{-1} , for **CI1-I** and **CI1-II**, respectively. These reaction barriers are slightly higher than the barrier of 72.2 kJ mol^{-1} obtained for the methyl CI (Figure 3). For the water-catalysed process we obtain reaction barriers of 54.0 and 53.0 kJ mol^{-1} , for **CI1-I** and **CI1-II**, respectively, relative to the free reactants. However, the reaction barriers relative to the reaction complexes **RC I** and **RC II** are 68.5 and 74.7 kJ mol^{-1} , respectively. These reaction barriers represent catalytic enhancements of 12.1 and 0.7 kJ mol^{-1} for **CI1-I** and **CI1-II**, respectively, compared to the uncatalysed pathways.

In the sulphuric acid-catalysed pathways, the RCs are associated with complexation energies of 87.5 and 86.4 kJ mol^{-1} for **CI1-I** and **CI1-II**, respectively. For comparison, in the water-catalysed reactions the corresponding complexation energies are 14.5 and 21.7 kJ mol^{-1} , respectively. Again, the very large complexation energies with H_2SO_4 are associated with fairly short $\text{SOH}\cdots\text{OO}$ hydrogen bond distances (of 1.339 and 1.407 \AA) and an electrostatic interaction between $\text{S}=\text{O}$ in H_2SO_4 and the β -hydrogen atom (of 2.492 and 2.384 \AA) for **CI1-I** and **CI1-II**. The transition structures for the sulphuric acid-catalysed 1,4-H transfers lie merely 25.3 and 24.5 kJ mol^{-1} above **RC I** and **RC II**, respectively. It is also important to note that the sulphuric acid-catalysed TSs lie well below the energies of the free reactants.

3.4 | Uncatalysed, water-catalysed, and sulphuric acid-catalysed 1,4 H-shift reaction of α -pinene Criegee intermediates

In this section, we consider the isomerization of CIs formed via α -pinene ozonolysis. Being endocyclic, the CI remains tethered to the molecule on rupturing of the primary ozonide. Consequently, two possible CI products are formed, which have available β -hydrogens. The structures for these CIs, labeled **CI1**, **CI2-I**, and **CI2-II** are shown in Figure 6. For each, we investigate 1,4 H-shift pathways with no catalyst, a H_2O catalyst, and a H_2SO_4 catalyst.

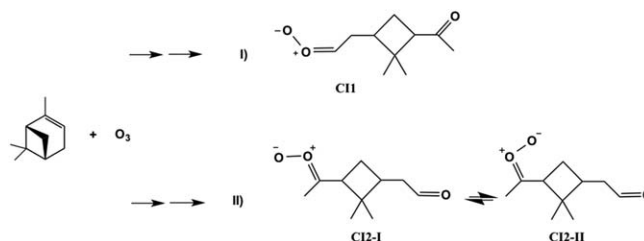


FIGURE 6 Formation of CIs via ozonolysis of α -pinene

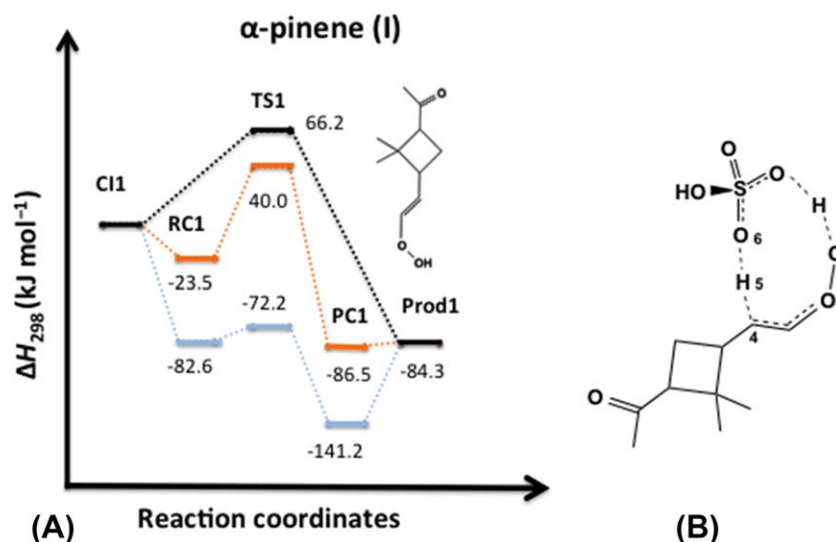


FIGURE 7 A, Reaction profiles (G4(MP2), ΔH_{298} , kJ mol^{-1}) for the uncatalysed (black line), water-catalysed (orange line), and sulphuric acid-catalysed (blue line) of 1,4 H-shifts of α -pinene **CI1**. B, Schematic representation of **TS1** catalysed by H_2SO_4

Figure 7 shows the reaction profile for the uncatalysed, water-catalysed, and sulphuric acid-catalysed 1,4 H-shifts in α -pinene **CI1**. The VHP channel is not possible for the *anti*-conformer of **CI1**, with previous theoretical work having shown 1,3-H transfers to be uncompetitive, and so this conformer is not considered in this study.^[7] The uncatalysed 1,4 H-shift reaction of **CI1** has a barrier height of 66.2 kJ mol^{-1} , which is lower in energy compared to the CH_3CHOO and the isoprene derived CI. The water-catalysed channel has a reaction barrier height (**TS1**) of 63.5 kJ mol^{-1} . Once again, this shows that water has a relatively small catalytic enhancement on the enthalpic energy surface. As shown in Figure 7, the energy difference between **TS1** and **RC1** in the sulphuric acid-catalysed pathway is merely 10.4 kJ mol^{-1} . This barrier is lower by 6.0 kJ mol^{-1} than the one in CH_3CHOO CI (Figure 3). Further inspection of these TSs indicates that the electrostatic interaction between S=O in H_2SO_4 and the β -hydrogen atom in **CI1** (of 1.381 \AA) is significantly stronger than the one in CH_3CHOO CI (of 2.363 \AA). This is also consistent with the APT charges for the α -pinene **TS1** being more pronounced than those for the CH_3CHOO CI. In particular, we obtain the following atomic charges for the α -pinene **TS1**: -0.451 (C^4), $+0.595$ (H^5), and -1.029 (O^6) a.u.

Both *syn*- and *anti*-conformers of the second CI structure (**CI2**) have accessible VHP channels. The enthalpic energy surfaces for the uncatalysed, water-catalysed, and sulphuric acid-catalysed reactions are shown in Figure 8. The **CI2-I** conformer is more stable than the **CI2-II** conformer by 17.5 kJ mol^{-1} , suggesting that steric effects play an important role. The channel involving the more stable *anti* conformer (**CI2-I**) is both

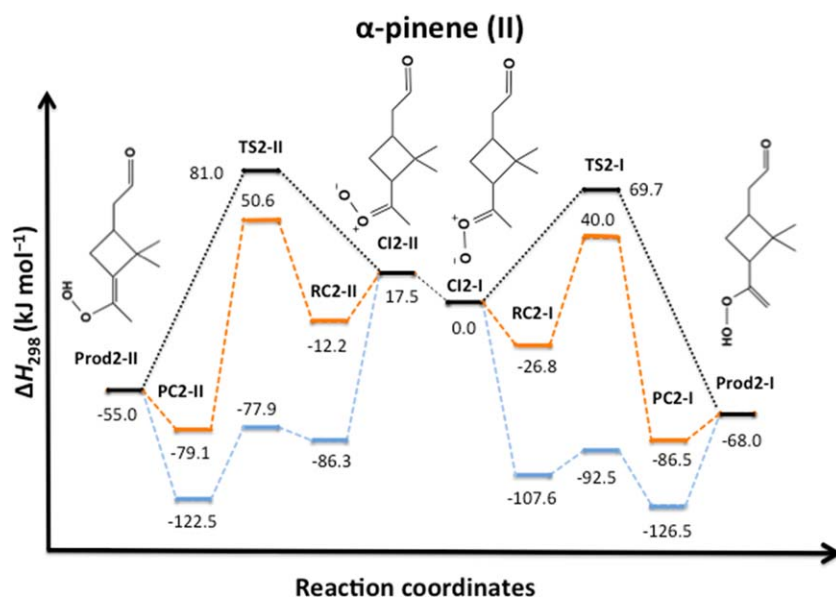


FIGURE 8 Reaction profiles (G4(MP2), ΔH_{298} , kJ mol^{-1}) for the uncatalysed (black line), water-catalysed (orange line), and sulphuric acid-catalysed (blue line) for the 1,4 H-shifts of α -pinene **CI2** (**CI2-I** and **CI2-II**)

kinetically and thermodynamically favorable. In particular, the reaction barrier height for the uncatalysed reaction is lower than the one for **C12-II** by 11.3 kJ mol^{-1} , and the *anti*-product (**Prod2-I**) is more stable than the *syn* product (**Prod2-II**) by 13.0 kJ mol^{-1} . These differences might be attributed to the fact that the 1,4-H shift from the more flexible methyl group is easier compared to that from a more rigid cyclic structure. Nonetheless, given that α -pinene CIs are formed with substantial excess energy,^[68] any energy difference is only likely to disrupt formation from stabilized CIs, of which the uncatalysed VHP channel is generally disregarded.

Figure 8 shows that a water catalyst provides little catalytic enhancement for 1,4-H shift reactions in **C12-I** and **C12-II**. This is consistent with the results for the other CIs. A sulphuric acid catalyst reduces the barriers for 1,4 H-isomerizations to 15.1 kJ mol^{-1} and 8.4 kJ mol^{-1} , for **C12-I** and **C12-II**, relative to their respective reaction complexes. These barriers are submerged with respect to the free reactants, creating a barrierless process. 1,4-H shift reactions catalysed by H_2SO_4 are, therefore, expected to occur at the kinetic limit, assuming no geometry hindrance. It is interesting to note that isoprene derived CIs, despite still having barrierless reaction profiles with an H_2SO_4 catalyst, have slightly higher barrier heights in the sulphuric acid-catalysed channel compared to α -pinene.

4 | CONCLUSIONS

Using the high-level G4(MP2) composite ab initio theoretical procedure, sulphuric acid was found to effectively catalyse 1,4 hydrogen shift reactions in methyl CI and in isoprene derived and α -pinene derived CIs. The reaction barrier heights for the sulphuric acid-catalysed reactions are 16.4 (methyl CI), 24.5 (isoprene CI), and 8.4 (α -pinene CI) kJ mol^{-1} , relative to the reactant complexes. Where in all cases the energies of the transition structures are well below the energies of the isolated CI and H_2SO_4 catalyst. Conversely, water was found to exhibit only a minor catalytic effect for these 1,4 H-shift reactions. Therefore, the computational findings presented here suggest the possibility of a facile bimolecular reaction of sulphuric acid with higher Criegee intermediates containing a β -hydrogen, resulting in the formation of vinyl hydroperoxide. Reaction with sulphuric acid is, therefore, likely an important removal process for stabilized CIs in regions of high H_2SO_4 concentrations. Ultimately such a mechanism would enhance tropospheric OH production. Considering the ubiquity of sulphuric acid in secondary organic aerosol formation, products formed through this channel are likely to directly contribute to organic aerosol production.

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REFERENCES

- [1] J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, G. Yarwood, in *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, New York/Oxford 2000.
- [2] D. Johnson, G. Marston, *Chem. Soc. Rev.* **2008**, *37*, 699.
- [3] M. Hallquist, J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, *Atmos. Chem. Phys.* **2009**, *9*, 5155.
- [4] L. Vereecken, D. R. Glowacki, M. J. Pilling, *Chem. Rev.* **2015**, *115*, 4063.
- [5] B. Chuong, J. Zhang, N. M. Donahue, *J. Am. Chem. Soc.* **2004**, *126*, 12363.
- [6] C. Yin, T. Kaito, *Phys. Chem. Chem. Phys.* **2017**, *19*, 12075.
- [7] L. Vereecken, J. S. Francisco, *Chem. Soc. Rev.* **2012**, *41*, 6259.
- [8] J. H. Kroll, J. H. Seinfeld, *Atmos. Environ.* **2008**, *42*, 3593.
- [9] R.W. Kugel, B. S. Ault, *J. Phys. Chem. A* **2015**, *119*, 312.
- [10] I. Barnes, J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, G. Yarwood, *J. Atmos. Chem.* **2001**, *39*, 328.
- [11] R. Atkinson, J. Arey, *Atmos. Environ.* **2003**, *37*, 197.
- [12] F. Liu, J. M. Beames, A. S. Petit, A. B. McCoy, M. I. Lester, *Science* **2014**, *345*, 1596.
- [13] C. C. Womack, M. A. Martin-Drumel, G. G. Brown, R. W. Field, M. C. McCarthy, *Sci. Adv.* **2015**, *1*, e1400105.
- [14] J. Ahrens, P. Carlsson, N. Hertl, M. Olzmann, M. Pfeifle, T. Wolf, Zeuch, *Angew. Chem. Int. Ed.* **2014**, *53*, 715.
- [15] E. Miliordos, S. S. Xantheas, *Angew. Chem. Int. Ed.* **2016**, *128*, 1027.

- [16] F. A. Mackenzie-Rae, A. Karton, S. M. Saunders, *Phys. Chem. Chem. Phys.* **2016**, *18*, 27991.
- [17] G. T. Drozd, J. Kroll, N. M. Donahue, *J. Phys. Chem. A* **2010**, *115*, 161.
- [18] M. Kulmala, J. Kontkanen, H. Junninen, K. Lehtipalo, H. E. Manninen, T. Nieminen, T. Petäjä, M. Sipilä, S. Schobesberger, P. Rantala, A. Franchin, *Science* **2013**, *339*, 943.
- [19] B. Long, J. L. Bao, D. G. Truhlar, *J. Am. Chem. Soc.* **2016**, *138*, 14409.
- [20] B. Chan, L. Radom, *J. Chem. Theory Comput.* **2015**, *11*, 2109.
- [21] A. Karton, *WIREs Comput. Mol. Sci.* **2016**, *6*, 292.
- [22] A. Karton, J. M. L. Martin *J. Chem. Phys.* **2012**, *136*, 124114.
- [23] M. Kumar, D. H. Busch, B. Subramaniam, W. H. Thompson, *Phys. Chem. Chem. Phys.* **2014**, *16*, 22968.
- [24] R. J. Buszek, J. S. Francisco, J. M. Anglada, *Int. Rev. Phys. Chem.* **2011**, *30*, 335.
- [25] M. Torrent-Sucarrat, J. S. Francisco, J. M. Anglada, *J. Am. Chem. Soc.* **2012**, *134*, 20632.
- [26] R. J. Buszek, A. Sinha, J. S. Francisco, *J. Am. Chem. Soc.* **2011**, *133*, 2013.
- [27] A. Karton, *Chem. Phys. Lett.* **2014**, *592*, 330.
- [28] C. R. Lin, L. J. Yu, S. Li, A. Karton, *Chem. Phys. Lett.* **2016**, *659*, 100.
- [29] F. Sarrami, L. J. Yu, W. Wan, A. Karton, *Chem. Phys. Lett.* **2016**, *675*, 27.
- [30] R. L. Mauldin Iii, T. Berndt, M. Sipilä, P. Paasonen, T. Petäjä, S. Kim, T. Kurtén, F. Stratmann, V. M. Kerminen, M. Kulmala, *Nature* **2012**, *488*, 193.
- [31] C. J. Percival, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, D. O. Topping, D. Lowe, S. R. Utembe, A. Bacak, G. McFiggans, M. C. Cooke, *Faraday Discuss.* **2013**, *165*, 45.
- [32] M. Boy, D. Mogensen, S. Smolander, L. Zhou, T. Nieminen, P. Paasonen, C. Plass-Dülmer, M. Sipilä, T. Petäjä, L. Mauldin, H. Berresheim, *Atmos. Chem. Phys.* **2013**, *13*, 3865.
- [33] S. Kim, A. Guenther, B. Lefer, J. Flynn, R. Griffin, A. P. Rutter, L. Gong, B. K. Cevik, *Environ. Sci. Technol.* **2015**, *49*, 3383.
- [34] C. Kuang, P. H. McMurry, A. V. McCormick, F. L. Eisele, *J. Geophys. Res. Atmos.* **2008**, *113*, D10209.
- [35] S. L. Sihto, M. Kulmala, V. M. Kerminen, M. D. Maso, T. Petäjä, I. Riipinen, H. Korhonen, F. Arnold, R. Janson, M. Boy, A. Laaksonen, *Atmos. Chem. Phys.* **2006**, *6*, 4079.
- [36] M. Sipilä, T. Berndt, T. Petäjä, D. Brus, J. Vanhanen, F. Stratmann, J. Patokoski, R. L. Mauldin, A. P. Hyvärinen, H. Lihavainen, M. Kulmala, *Science* **2010**, *327*, 1243.
- [37] A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. McKay, T. Pierce, *J. Geophys. Res. Atmos.* **1995**, *100*, 8873.
- [38] A. B. Guenther, X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, X. Wang, *Geosci. Model Dev.* **2012**, *5*, 1471.
- [39] N. C. Eddingsaas, C. L. Loza, L. D. Yee, M. Chan, K. A. Schilling, P. S. Chhabra, J. H. Seinfeld, P. O. Wennberg, *Atmos. Chem. Phys.* **2012**, *12*, 7413.
- [40] M. Camredon, J. F. Hamilton, M. S. Alam, K. P. Wyche, T. Carr, I. R. White, P. S. Monks, A. R. Rickard, W. J. Bloss, *Atmos. Chem. Phys.* **2010**, *10*, 2893.
- [41] K. M. Henry, T. Lohaus, N. M. Donahue, *Environ. Sci. Technol.* **2012**, *46*, 12347.
- [42] Y. Sakamoto, S. Inomata, J. Hirokawa, *J. Phys. Chem. A* **2013**, *117*, 12912.
- [43] Y. Sakamoto, R. Yajima, S. Inomata, J. Hirokawa, *Phys. Chem. Chem. Phys.* **2017**, *19*, 3165.
- [44] Y. Zhao, L. M. Wingen, V. Perraud, J. Greaves, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2015**, *17*, 12500.
- [45] M. Ehn, J. A. Thornton, E. Kleist, M. Sipilä, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, *Nature* **2014**, *506*, 476.
- [46] T. Jokinen, T. Berndt, R. Makkonen, V. M. Kerminen, H. Junninen, P. Paasonen, F. Stratmann, H. Herrmann, A. B. Guenther, D. R. Worsnop, M. Kulmala, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 7123.
- [47] T. Kurtén, M. P. Rissanen, K. Mackeprang, J. A. Thornton, N. Hyttinen, S. Jørgensen, M. Ehn, H. G. Kjaergaard, *J. Phys. Chem. A* **2015**, *119*, 11366.
- [48] J. M. Anglada, J. Gonzalez, M. Torrent-Sucarrat, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13034.
- [49] L. Jiang, Y. S. Xu, A. Z. Ding, *Int. J. Mol. Sci.* **2013**, *14*, 5784.
- [50] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **2007**, *127*, 124105.
- [51] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *WIREs Comput. Mol. Sci.* **2011**, *1*, 810.
- [52] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **2005**, *123*, 124107.
- [53] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *Chem. Phys. Lett.* **2010**, *499*, 168.
- [54] A. Karton, R. J. O'Reilly, L. Radom, *J. Phys. Chem. A* **2012**, *116*, 4211.
- [55] A. Karton, L. Goerigk, *J. Comput. Chem.* **2015**, *36*, 622.
- [56] L. J. Yu, F. Sarrami, R. J. O'Reilly, A. Karton, *Chem. Phys.* **2015**, *458*, 1.
- [57] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford, CT **2009**.
- [58] C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154.

- [59] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.
- [60] K. T. Kuwata, L. C. Valin, A. D. Converse, *J. Phys. Chem. A* **2005**, *109*, 10710.
- [61] J. A. Montgomery Jr, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532.
- [62] Y. Fang, F. Liu, V. P. Barber, S. J. Klippenstein, A. B. McCoy, M. I. Lester, *Chem. Phys.* **2016**, *144*, 061102.
- [63] N. M. Kidwell, H. Li, X. Wang, J. M. Bowman, M. I. Lester, *Nat. Chem.* **2016**, *8*, 509.
- [64] R. Gutbrod, E. Kraka, R. N. Schindler, D. Cremer, *J. Am. Chem. Soc.* **1997**, *119*, 7330.
- [65] G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441.
- [66] J. Cioslowski, *J. Am. Chem. Soc.* **1989**, *111*, 8333.
- [67] F. De Proft, J. M. L. Martin, P. Geerlings, *Chem. Phys. Lett.* **1996**, *250*, 393.
- [68] D. Zhang, R. Zhang, *J. Chem. Phys.* **2005**, *122*, 114308.

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