

Theoretical studies of the hydration reactions of stabilized Criegee intermediates from the ozonolysis of β -pinene

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A theoretical study was performed of the reactions of the stabilized Criegee intermediates (sCIs) of β -pinene with H_2O and its dimer. Due to the large size of the biogenic sCIs, the transition states of the hydration reactions were explored with the Monte Carlo Transition State Search Program (MCTSSP), which integrated the Monte Carlo sampling technique with a transition state optimization method. The computations were performed with the M06-2X/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) levels of theory. The relative energies showed that the results of the M06-2X functional are in good agreement with the results of the DF-MP2 and CCSD(T) methods. Both the reactions of the β -pinene-sCI with H_2O and the β -pinene-sCI with $(\text{H}_2\text{O})_2$ were found to be strongly exothermic. Activation barrier calculations indicate that the sink reaction with the water dimer may proceed significantly faster than the reaction with the water monomer despite the low concentration of water dimers in the atmosphere. Therefore, the reaction of sCIs with water vapor that includes large water clusters rather than single water molecules should be studied.

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1. Introduction

The amount of unsaturated hydrocarbons emitted into the atmosphere is estimated to be more than 630 Tg C per year.¹ The reaction of ozone with alkenes, which is known as ozonolysis and which can produce significant quantities of secondary organic aerosols, is one of the most important oxidation reactions in the troposphere.²⁻⁸ The carbonyl oxides, which are also called Criegee intermediates (CIs), are key intermediates in the reaction of ozone with alkenes.^{4,9} The fate of a CI is either to decompose unimolecularly or to be vibrationally stabilized. Stabilized Criegee intermediates (sCIs) can further react with other atmospheric species such as water vapor, NO_2 , SO_2 , oxygenates *etc.*¹⁰⁻¹⁶ One of the most important reactions in atmospheric chemistry is the reaction of sCIs with water because of the high quantity of water vapor in Earth's atmosphere.¹³ The reaction between sCIs and water produces α -hydroxy-hydroperoxides (HMHPs), which have been detected in the atmosphere and which have a direct impact on forest damage.^{5,17-21} HMHP can undergo subsequent reactions such as decomposing or reacting with other atmospheric species to produce H_2O_2 , organic acids, aldehydes and ketones.^{17,18,20,22-25}

The reaction of sCIs with water is also an essential source of OH radicals.^{22,23} Moreover, the oxidation of water by stabilized Criegee intermediates from the ozonolysis of alkenes can influence the formation of new particles.²⁶⁻²⁸ Boris Bonn *et al.*^{29,30} found a decrease in both the particle number concentration and the total aerosol volume with increasing water vapor or formic acid. The water dimer^{31,32} can also react with a sCI, and this reaction was found to have a lower activation barrier than the reaction of a sCI with a single water molecule,^{33,34} a result that can significantly influence the overall sCI-water reaction.

Theoretical studies of the reactions of several carbonyl oxides with water and water dimers have been reported in the literature,^{13,22,33-36} but most of the studies were of small Criegee intermediates, especially the simplest parent carbonyl oxide (H_2COO). However, small CIs such as H_2COO have very short lifetimes and cannot be significantly stabilized at atmospheric pressure, whereas larger CIs, which contain more carbon atoms, can be stabilized; *e.g.*, the CI of β -pinene can be stabilized at 40% at 1 atm.³⁵⁻³⁷ Because β -pinene is one of the most abundant biogenic volatile organic compounds (BVOCs), many experimental and theoretical works concerning the ozonolysis of β -pinene have been carried out.^{35,38-45} The reaction mechanisms of the large sCIs of β -pinene and in particular the bimolecular reactions have seldom been investigated to the best of our knowledge.

In the present study, the reactions of the large sCIs from the ozonolysis of β -pinene with water and its dimer have been

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investigated. The most favorable mechanism involves the reaction of the sCIs with water, and reactions with the water dimer were considered to lead to the formation of organic peroxides.^{19,33,34} With the hydration reactions of large biogenic sCIs, finding the lowest-energy structure of the transition states by manual search is challenging. The transition state corresponding to the lowest-energy path is particularly important for the study of the kinetics and mechanism of chemical reactions. To overcome this difficulty, we developed a program called the Monte Carlo Transition State Search Program (MCTSSP) to find the transition states (TSs). DFT methods have been employed to obtain the geometries and energies of the TSs, the hydrogen-bonded complexes and the corresponding α -hydroxy hydroperoxide (HMHP) products. The performances of the M06-2X and B3LYP geometries and energies in the reactions of the large biogenic sCIs have been compared. A thermochemical analysis has been conducted, and its results and the implications to atmospheric chemistry are also analyzed.

2. Computational details

2.1. Monte Carlo Transition State Search Program (MCTSSP)

Our successful Basin-Hopping program has been widely used in the exploration of the structures of atomic and molecular clusters.^{46–55} We have since developed a new program called the Monte Carlo Transition State Search Program (MCTSSP) to automatically search for the TSs of complex atmospheric reactions. The MCTSSP combines the Monte Carlo sampling technique and a local TS optimization method using an efficient computer script. This new technique simplifies the time-consuming and tedious procedure of manual search and makes the search for the transition state more convenient and efficient.

When running MCTSSP, only the reactant structures are needed as initial inputs for the Monte Carlo random sampling; *a priori* knowledge of the products is not required. The program for finding TSs can be summarized as follows:

- (1) Input the known reactants structure (Cartesian coordinates of reactant A and reactant B) and some simple parameters. (Sampling parameter R represents a minimal distance between atoms, M represents the number of TS searches.)

- (2) Start from the given reactants structure, the initial random guess is generated automatically *via* Monte Carlo sampling.

- (3) Invoke Gaussian 09 (or other quantum chemistry package) to optimize the initial guess and calculate the frequency with low-cost electronic structure methods such as HF or DFT (method and basis set are set by the users in step (1)).

- (4) Read the output frequencies. If the list of output frequencies has only one imaginary frequency (IF), then the optimized geometries with sampling parameter $R = R'$ are saved, and $R = R'$ replaces $R = R_0$ as the minimal distance in the next cycle. If not, sampling continues with parameter $R = R_0$ until the structure with only one IF is found.

- (5) Terminate the search. The TS searching number M is set to terminate the program. M defined by the user is based on the size of the system. If the value of M is large enough, the program will repeatedly find the same TSs, and if M is set to only 1, many

TSs will be lost. To solve this issue, we can perform MCTSSP for several runs until no new TS structures are found.

In this paper, we used the MCTSSP to explore all of the TSs of the reactions of the sCI of β -pinene with water and the water dimer. To find each TS within a short period of time, we selected the low-level HF/6-31+G(d) theory for the initial search, and this theory proved to be adequate.

2.2. Electronic structure and stationary-point energy calculations

The TSs obtained from the MCTSSP using the low-level HF/6-31+G(d) theory are rough structures, and further higher-level structural optimizations should be conducted. The geometries of the reactants, H-bonded complexes, transition states and products of the reactions of the sCIs with H_2O and $(\text{H}_2\text{O})_2$ were optimized using B3LYP^{56,57} and M06-2X⁵⁸ with the 6-311+G(2d,p) basis set. Diffuse and extra p-type polarization functions were added to better describe the possible hydrogen bonding of water with the sCIs of β -pinene. The hybrid density functional B3LYP is the most widely used functional in the study of chemical reactions.^{59,60} In recent studies, the M06-2X functional has been shown to perform well in thermochemical and reaction mechanism studies, especially in studies of non-bonded complexes.^{61–64} Test calculations of the effects of the basis set size on the energetic and geometric parameters by Bo Long *et al.*⁶⁵ in the study of the reaction of stabilized H_2COO with HO_2 and the $\text{HO}_2 \cdots \text{H}_2\text{O}$ complex showed that the effects of the basis set size are of minor importance. An assessment by Theo Kurtén *et al.*⁶⁶ of large biogenic stabilized Criegee intermediates and sulfuric acid also suggested that energetics are not strongly affected by the basis set. Hence, in the present work, we chose M06-2X and B3LYP functionals with the 6-311+G(2d,p) basis set to study the hydration reactions of the sCIs of β -pinene.

All of the stationary points were characterized using harmonic vibrational frequency calculations. Local minima showed all positive frequencies, and transition states were characterized as first-order saddle points with a single imaginary frequency. With the reactions studied here, intrinsic reaction coordinate (IRC) calculations on all of the relevant TSs were performed to verify the connectivity between a given transition state and the corresponding reactants and products. The DFT structures were then used in the single-point energy calculations using density fitting frozen core second-order Møller–Plesset perturbation theory (DF-MP2)⁶⁷ and coupled-cluster theory with single and double excitations including perturbative corrections for the triple excitations (CCSD(T)) theory.^{68,69} Automatic transition state searching was performed using the MCTSSP. Further electronic structure optimizations of all of the species were performed using the Gaussian 09 package.⁷⁰ Highly accurate single-point energy calculations were performed using Molpro 2010.1.^{71,72}

3. Results and discussion

3.1. Structural and energy analyses

To assess the performance of the chosen B3LYP and M06-2X methods, the structures and energies of the reactants, products

and TSs were analyzed. The optimized structures of the reactants, products and TSs of the reactions of the sCI1 of β -pinene with H_2O and of the sCI2 of β -pinene with H_2O are presented in Fig. 1 and 2, respectively. Shown in Fig. 3 are the structures of the corresponding hydrogen-bonded complexes, which were obtained by optimizing the final structures from the IRC calculations on the reactant side. The structural parameters of the most reactive species obtained from the B3LYP/6-311+G(2d,p) and M06-2X/6-311+G(2d,p) calculations differ slightly. For instance, the average root mean square deviation (RMSD) between the internal coordinates obtained from the B3LYP and M06-2X methods is 0.04 Å for the reactants, 0.05 Å for the transition states and 0.04 Å for the products. However, the RMSD between the internal coordinates obtained using the B3LYP and M06-2X methods is 0.17 Å for the hydrogen-bonded complexes. It has been reported in a recent study that M06-2X can describe noncovalent interactions such as the distance between weakly bound molecules, whereas plain hybrid density functionals such as B3LYP often yield qualitatively incorrect results for long-range molecular interactions.^{58,63,73} In Table 1, the relevant bond lengths of the hydrogen-bonded complexes that were investigated using the B3LYP and M06-2X methods are shown. Most of the bond lengths calculated using the B3LYP and M06-2X functionals are comparable; the bond lengths differ by less than 0.02 Å except for the long-range interaction distance of ($\text{H}^{\text{water}} \cdots \text{O}^{\text{sCI}}$) $\text{O}_2\text{-H}_w$. The results indicate that non-covalent interactions may be the major cause of the differences in the geometric parameters between B3LYP and M06-2X.

Although most of the structural parameters obtained from the B3LYP and M06-2X calculations differ only slightly, the relative energies shown in Tables 2 and 3 show that there are

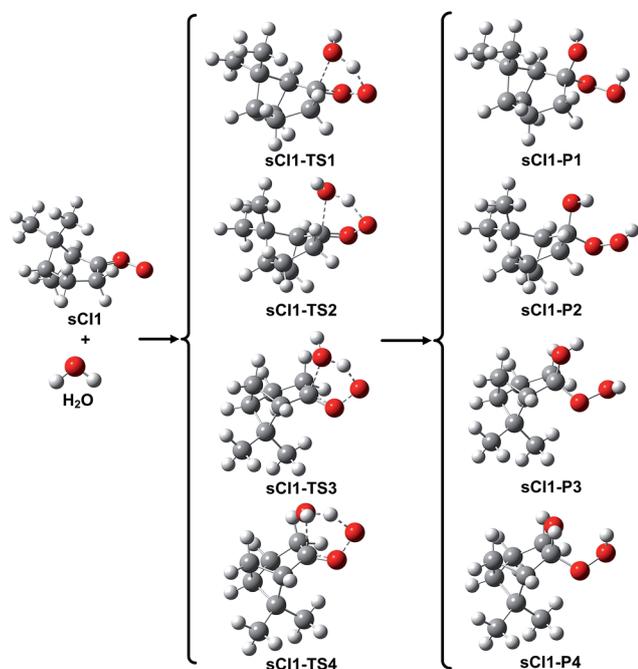


Fig. 1 Optimized geometries of the reactants, products, and transition states (TSs) of the reaction of the sCI1 of β -pinene with H_2O .

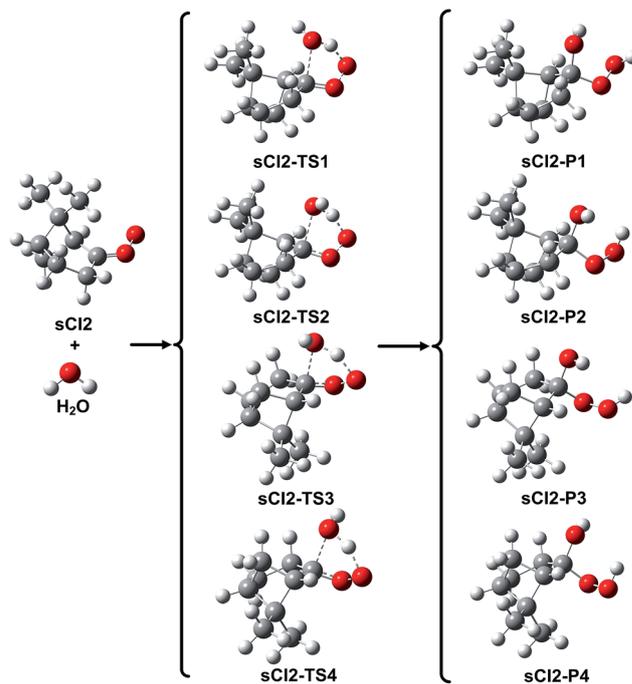


Fig. 2 Optimized geometries of the reactants, products, and transition states (TSs) of the reaction of the sCI2 of β -pinene with H_2O .

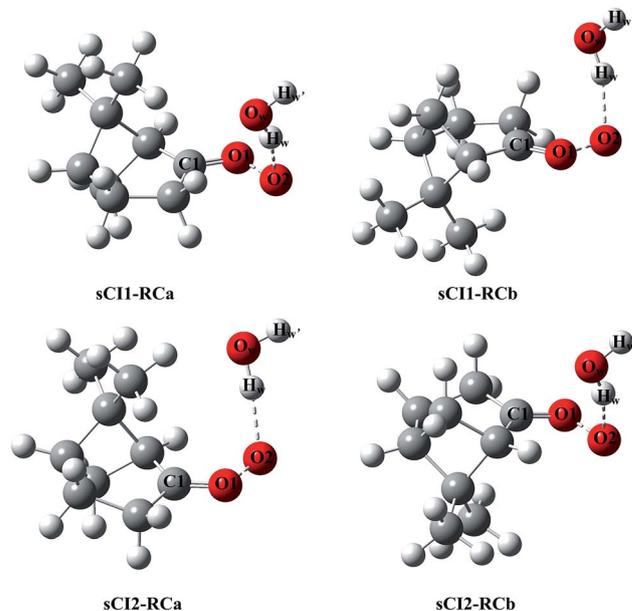


Fig. 3 Optimized geometries of the reactant complexes (RC) of the reactions of the sCI1 of β -pinene with H_2O and the sCI2 of β -pinene with H_2O .

greater differences between the M06-2X/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) methods. The binding energies and activation barriers (with respect to the corresponding hydrogen-bonded complexes) predicted by the two methods differ by ~ 3 kcal mol⁻¹ for the reaction of the sCI of β -pinene with H_2O . The differences in the reaction energies that were calculated using

Table 1 The selected bond lengths of the reactant complexes that were found with the B3LYP/6-311+G(2d,p) and M06-2X/6-311+G(2d,p) levels of theory (bond distances in angstroms)

Bond	B3LYP/6-311+G(2d,p)				M06-2X/6-311+G(2d,p)			
	sCI1-RCa	sCI1-RCb	sCI2-RCa	sCI2-RCb	sCI1-RCa	sCI1-RCb	sCI2-RCa	sCI2-RCb
C1–O1	1.261	1.262	1.261	1.260	1.250	1.249	1.249	1.248
O1–O2	1.408	1.408	1.409	1.411	1.393	1.394	1.393	1.399
O2–H _w	1.769	1.763	1.755	1.769	1.743	1.784	1.722	1.787
O _w –H _w	0.987	0.987	0.987	0.987	0.985	0.983	0.986	0.984
O _w –H _w	0.962	0.962	0.962	0.962	0.959	0.959	0.959	0.959

Table 2 The relative energy (ΔE in kcal mol⁻¹), relative enthalpy (ΔH in kcal mol⁻¹) and Gibb's free energy (ΔG in kcal mol⁻¹) of the stationary points on the ground-state potential energy surface of the reactions of the sCIs of β -pinene (sCI1 and sCI2) with H₂O that were calculated with the B3LYP/6-311+G(2d,p) level of theory including zero-point corrections at 298 K

Compound	ΔE	ΔH	ΔG
sCI1 + H ₂ O	0.00	0.00	0.00
sCI1-RCa	-7.95	-8.55	0.60
sCI1-RCb	-8.02	-8.61	0.39
sCI1-TS1	8.67 (16.62) ^b	8.07	20.33
sCI1-TS2	11.03 (18.98) ^b	10.43	22.82
sCI1-TS3	9.06 (17.08) ^b	8.47	20.69
sCI1-TS4	6.72 (14.74) ^b	6.13	18.37
sCI1-P1	-22.79	-22.38	-11.56
sCI1-P2	-21.68	-22.27	-11.01
sCI1-P3	-21.63	-22.23	-11.05
sCI1-P4	-23.01	-23.61	-11.80
sCI2 + H ₂ O	0.0 (2.6) ^a	0.0 (2.6) ^a	0.0 (2.5) ^a
sCI2-RCa	-5.53	-6.13	2.81
sCI2-RCb	-5.07	-5.66	3.08
sCI2-TS1	8.44 (13.97) ^b	7.85	20.41
sCI2-TS2	7.73 (13.26) ^b	7.14	19.62
sCI2-TS3	6.62 (11.69) ^b	6.03	18.47
sCI2-TS4	5.98 (11.05) ^b	5.38	17.71
sCI2-P1	-23.15	-23.74	-12.13
sCI2-P2	-22.76	-23.35	-11.67
sCI2-P3	-22.96	-23.55	-11.91
sCI2-P4	-22.68	-23.27	-11.63

^a The value in parentheses is the energy of the sCI2 + H₂O relative to the energy of the sCI1 + H₂O. ^b The values in parentheses are the activation barriers with respect to the corresponding reactant complexes.

Table 3 The relative energy (ΔE in kcal mol⁻¹), relative enthalpy (ΔH in kcal mol⁻¹) and Gibb's free energy (ΔG in kcal mol⁻¹) of the stationary points on the ground-state potential energy surface of the reactions of the sCIs of β -pinene (sCI1 and sCI2) with H₂O that were calculated with the M06-2X/6-311+G(2d,p) level of theory including zero-point corrections at 298 K

Compound	ΔE^a	ΔH	ΔG
sCI1 + H ₂ O	0.0	0.0	0.0
sCI1-RCa	-11.43	-12.02	-1.95
sCI1-RCb	-11.05	-11.64	-2.04
sCI1-TS1	3.06 (14.49) ^b	2.47	15.21
sCI1-TS2	5.15 (16.58) ^b	4.56	17.38
sCI1-TS3	3.53 (14.58) ^b	2.94	15.27
sCI1-TS4	1.16 (12.21) ^b	0.57	13.00
sCI1-P1	-36.08	-36.68	-24.41
sCI1-P2	-34.72	-35.32	-23.23
sCI1-P3	-34.58	-35.18	-23.58
sCI1-P4	-35.96	-36.55	-24.26
sCI2 + H ₂ O	0.0 (2.2) ^a	0.0 (2.2) ^a	0.0 (2.3) ^a
sCI2-RCa	-11.38	-9.75	0.38
sCI2-RCb	-10.86	-9.23	0.69
sCI2-TS1	0.38 (11.76) ^b	2.01	15.03
sCI2-TS2	-0.24 (11.14) ^b	1.39	14.27
sCI2-TS3	-1.38 (9.48) ^b	0.25	13.06
sCI2-TS4	-1.93 (8.93) ^b	-0.30	12.42
sCI2-P1	-38.32	-36.69	-24.75
sCI2-P2	-37.97	-36.34	-24.30
sCI2-P3	-37.99	-36.36	-24.36
sCI2-P4	-38.07	-36.44	-24.22

^a The value in parentheses is the energy of the sCI2 + H₂O relative to the energy of the sCI1 + H₂O. ^b The values in parentheses are the activation barriers with respect to the corresponding reactant complexes.

the two methods are more than 10 kcal mol⁻¹. To assess the reliability of the DFT results, the relative energies have also been calculated using the DF-MP2 and CCSD(T) methods. We have chosen to discuss the sCI1 of β -pinene, and the results are summarized in Tables 4 and 5. The calculated relative energy values show that the results of M06-2X are comparable with those obtained with the DF-MP2/6-311++G(3df,2p)//M06-2X/6-311+G(2d,p) and CCSD(T)/6-31G(d)//M06-2X/6-311+G(2d,p) levels. However, the relative energies calculated with the B3LYP/6-311+G(2d,p) level of theory differ significantly when compared with the DF-MP2 and CCSD(T) results. Interestingly, the relative energy values at the CCSD(T)/6-31G(d)//M06-2X/6-311+G(2d,p) or DF-MP2/6-311++G(3df,2p)//M06-2X/6-311+G(2d,p) level are

in fairly good agreement with the values from the CCSD(T)/6-31G(d)//B3LYP/6-311+G(2d,p) or DF-MP2/6-311++G(3df,2p)//B3LYP/6-311+G(2d,p) level of theory. This indicates that the M06-2X functional outperforms the B3LYP functional in describing the interaction energies of the sCI of β -pinene with the water molecule. Therefore, the M06-2X functional is suitable for the reactions of biogenic sCIs with water and water dimers.

3.2. Reactions of the sCI of β -pinene with water

The reactions between carbonyl oxides and water are assumed to begin with the formation of a pre-reactive hydrogen-bonded complex that occurs before the transition state and the α -

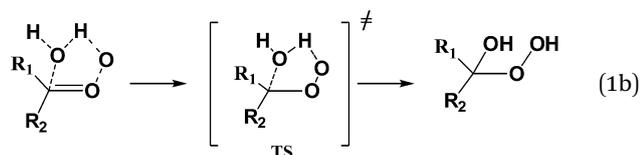
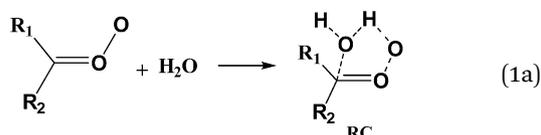
Table 4 The relative energies (0 K, $\Delta(E + \text{ZPE})$ in kcal mol⁻¹) computed using the B3LYP/6-311+G(2d,p) geometries of the hydration reaction of the sCI1 of β -pinene with water

Species	B3LYP/6-311+G(2d,p)	DF-MP2/6-311++G(3df,2p)	CCSD(T)/6-31G(d)
sCI1 + H ₂ O	0.0	0.0	0.0
sCI1-RCa	-8.14	-10.61	-11.24
sCI1-RCb	-8.21	-10.37	-10.56
sCI1-TS1	9.64	3.99	3.85
sCI1-TS2	12.04	6.12	6.41
sCI1-TS3	10.05	4.10	4.64
sCI1-TS4	7.72	1.91	1.89
sCI1-P1	-22.04	-36.30	-35.86
sCI1-P2	-21.10	-35.26	-34.43
sCI1-P3	-21.08	-35.38	-34.33
sCI1-P4	-22.27	-36.59	-36.07

Table 5 The relative energies (0 K, $\Delta(E + \text{ZPE})$ in kcal mol⁻¹) computed using the M06-2X/6-311+G(2d,p) geometries of the hydration reaction of the sCI1 of β -pinene with water

Species	M06-2X/6-311+G(2d,p)	DF-MP2/6-311++G(3df,2p)	CCSD(T)/6-31G(d)
sCI1 + H ₂ O	0.0	0.0	0.0
sCI1-RCa	-11.38	-10.41	-11.18
sCI1-RCb	-11.07	-10.45	-11.13
sCI1-TS1	4.23	5.02	4.45
sCI1-TS2	6.36	7.14	7.05
sCI1-TS3	4.59	4.85	4.93
sCI1-TS4	2.24	2.63	2.07
sCI1-P1	-35.16	-35.57	-35.32
sCI1-P2	-33.87	-34.39	-33.55
sCI1-P3	-33.90	-34.60	-33.57
sCI1-P4	-35.05	-35.69	-35.33

hydroxy hydroperoxide products.^{19,33,74,75} The reaction of the stabilized Criegee intermediate and H₂O proceeds as shown in reactions (1a) and (1b):



The B3LYP and M06-2X calculations that were conducted in this paper show that there are four different reaction pathways of the reaction of each sCI of β -pinene with H₂O. The reaction of a sCI of β -pinene with H₂O involves the transfer of one hydrogen atom of water to the terminal oxygen of the carbonyl oxide and simultaneously, the addition of the oxygen atom of water to the carbon atom of the carbonyl oxide (see Fig. 1 and 2). Generally, in the reaction of the sCI with water, the formation of the reactant complexes (RCs) occurs by hydrogen bond interactions

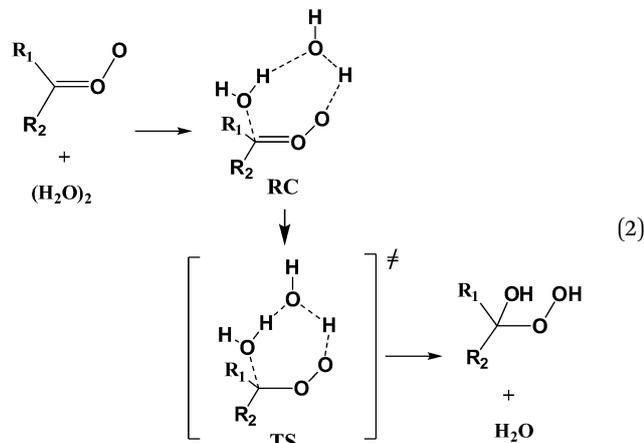
between the H atom of water and the O atom in the corresponding carbonyl oxide. In several cases, more than one channel leads to the same reactant complex. For example, CI1-TS1 and CI1-TS2 correspond to the same hydrogen-bonded complex (CI1-RCa); likewise, CI1-TS3 and CI1-TS4 correspond to the same hydrogen-bonded complex (CI1-RCb). Thus, there are two hydrogen-bonded complexes, CI1-RCa and CI1-RCb, from the reaction of the sCI1 with H₂O and two hydrogen-bonded complexes, CI2-RCa and CI2-RCb, from the reaction of the sCI2 with H₂O.

Tables 2 and 3 show the relative energy (ΔE in kcal mol⁻¹), the relative enthalpy (ΔH in kcal mol⁻¹) and the Gibbs free energy (ΔG in kcal mol⁻¹) of the separated sCI of β -pinene and H₂O at 298 K computed with the B3LYP/6-311+G(2d,p) and M06-2X/6-311+G(2d,p) levels of theory. The values in parentheses represent the energy of the sCI2 of β -pinene relative to the energy of the sCI1 of β -pinene. The energy of the sCI2 is approximately 2 kcal mol⁻¹ higher than that of the sCI1, which indicates that the sCI1 is more stable than the sCI2. Interestingly, the relative energy (2.2 kcal mol⁻¹) obtained with M06-2X/6-311+G(2d,p) is in fairly good agreement with the value (2.2 kcal mol⁻¹) calculated at the CBS-QB3//B3LYP/6-311G(d,p) level, which is as T. L. Nguyen, J. Peeters and L. Vereecken predicted.³⁵ The reactions of the sCIs of β -pinene with H₂O are strongly exothermic, as indicated by the ΔH (298 K) and ΔG (298 K) values. In the B3LYP/6-311+G(2d,p) calculation, the TSs are

computed to exist between 11.05 and 18.98 kcal mol⁻¹ above the corresponding reactant complexes (Table 2). In the reaction of H₂COO with water, the activation energy computed at the B3LYP/6-31G(d,p) level by Aplincourt *et al.*¹³ is only 6.7 kcal mol⁻¹. The activation energy of the sCI of β -pinene with water is much higher than the energy barrier of the reaction of H₂COO with water when employing the B3LYP method without considering basis set effects. This is probably attributed to the effects of the large cycloalkyl group. The electron donor character of the cycloalkyl group hinders the nucleophilic attack of the oxygen atom of water, which results in an increase in the reaction energy barrier. The effect of the substituents in the reactivity of the carbonyl oxides is also reflected in the reactions of the two conformers (sCI1 of β -pinene and sCI2 of β -pinene) with water. In the reaction of the sCI1 of β -pinene (the *anti* configuration) with H₂O, Table 2 shows that the computed binding energy of the complexes is 8 kcal mol⁻¹ and that the transition states lie between 6.72 and 11.03 kcal mol⁻¹ above the energy of the reactants. In the reaction of the sCI2 of β -pinene (the *syn* configuration), the complex has a binding energy of 5 kcal mol⁻¹, and the transition state lies between 5.98 and 8.44 kcal mol⁻¹ above the energy of the reactants. In the case of the M06-2X/6-311+G(2d,p) calculation, the energies of some of the TSs of the reaction of the sCI2 of β -pinene (the *syn* configuration) even lie below the energies of the reactants. As J. M. Anglada *et al.* discussed,⁵ both the nature of the substituent and its position (*syn* or *anti*) play a fundamental role in the reactivity of the carbonyl oxides.

3.3. Reactions of the sCI of β -pinene with the water dimer

The weakly bonded pairs of water molecules, (H₂O)₂, that have been experimentally detected in the atmosphere³¹ can also react with sCIs. Ryzhkov and Ariya^{33,34} have predicted that at 303 K and 100% RH, (H₂O)₂ reacts with the simplest parent CI (CH₂OO) almost 3 orders of magnitude faster than H₂O does. However, because of their low number, water clusters with three or more water molecules play no significant role in the overall reaction with sCIs.⁷⁶ Here, we consider the potentially



important reactions of the water dimer with the sCI of β -pinene. We suggest the additional channel of organic peroxide formation that was proposed by Andrew B. Ryzhkov and Parisa A. Ariya.^{33,34}

In the reaction of the sCI of β -pinene with the water dimer, we have chosen to discuss the more stable sCI1 of β -pinene. The TSs of the reaction of the sCI1 + (H₂O)₂ were found automatically using the MCTSSP. The reaction between the sCI of β -pinene and (H₂O)₂ proceeds *via* eight reaction pathways. The geometries of the reactants, TSs and hydrogen-bonded complexes that were optimized with M06-2X/6-311+G(2d,p) are displayed in Fig. 4 and 5. This hydration reaction produces a water monomer (reaction (2)). The sCI1-TS_d1 and sCI1-TS_d3 structures correspond to the same product structure sCI1-P1 (in Fig. 1) and water. The products sCI1-P1 and water were obtained by optimizing the final structures from the IRC calculations on the product side. This search was performed with all of the transition states. Likewise, sCI1-TS_d2 and sCI1-TS_d4, sCI1-TS_d5 and sCI1-TS_d7, and sCI1-TS_d6 and sCI1-TS_d8 correspond to the products of sCI1-P2 and water, sCI1-P3 and water, and sCI1-P4 and water, respectively.

The relative energy (ΔE), relative enthalpy (ΔH) and Gibb's free energy (ΔG) including a zero-point correction at 298 K of the reactions of the sCI of β -pinene with the water dimer are summarized in Table 6. The reaction energies range between -30.98 and -32.48 kcal mol⁻¹. The ΔH and ΔG values that were calculated with the M06-2X/6-311+G(2d,p) method show that the reaction is endothermic in the range of -30.98 to -32.48 kcal mol⁻¹ and exothermic in the range of -26.28 to

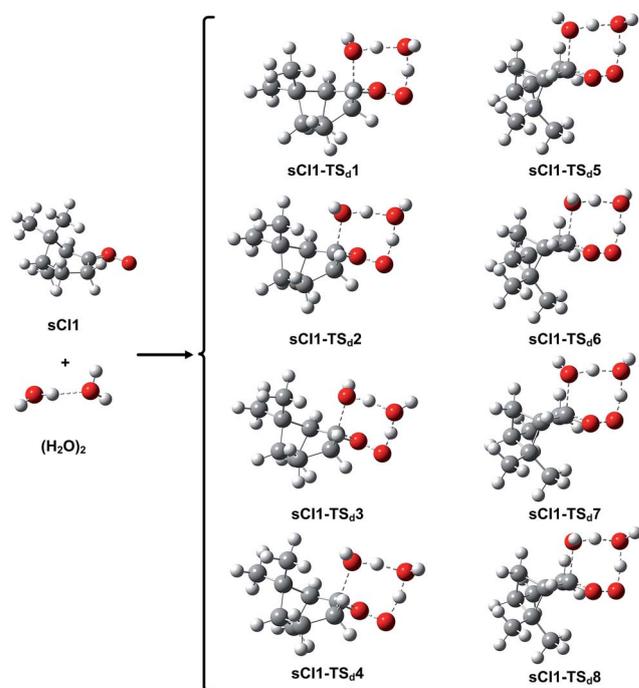


Fig. 4 Structures of the reactants and transition states (TSs) of the reaction of the sCI1 of β -pinene with (H₂O)₂ that were optimized with the M06-2X/6-311+G(2d,p) level of theory.

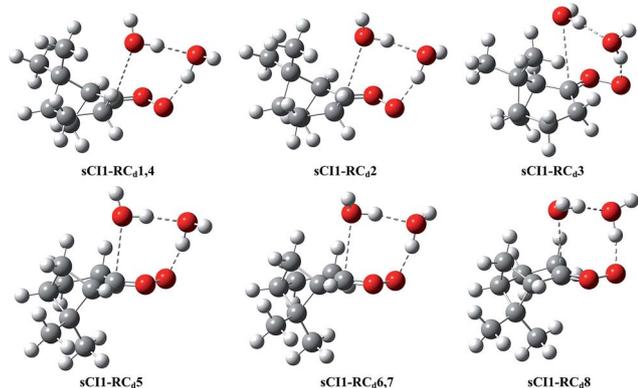


Fig. 5 Structures of the reactant complexes of the reaction of the sCI1 of β -pinene with $(\text{H}_2\text{O})_2$ that were optimized with the M06-2X/6-311+G(2d,p) level of theory.

Table 6 The relative energy (ΔE in kcal mol $^{-1}$), relative enthalpy (ΔH in kcal mol $^{-1}$) and Gibbs free energy (ΔG in kcal mol $^{-1}$) of the stationary points on the ground-state potential energy surface of the reactions of the sCI1 of β -pinene with $(\text{H}_2\text{O})_2$ that were calculated with the M06-2X/6-311+G(2d,p) level of theory including zero-point corrections at 298 K

Compound	ΔE^a	ΔH	ΔG
sCI1 + $(\text{H}_2\text{O})_2$	0.0	0.0	0.0
sCI1-RC _d (ref. 1 and 4)	-15.14	-15.73	-3.21
sCI1-RC _{d2}	-15.39	-15.98	-3.74
sCI1-RC _{d3}	-17.06	-17.65	-4.28
sCI1-RC _{d5}	-17.74	-18.34	-5.61
sCI1-RC _d (ref. 6 and 7)	-17.47	-18.06	-5.56
sCI1-RC _{d8}	-17.99	-18.58	-5.75
sCI1-TS _{d1}	-7.18 (7.96)	-7.77	8.38
sCI1-TS _{d2}	-7.45 (7.94)	-8.04	8.56
sCI1-TS _{d3}	-7.87 (9.19)	-8.46	8.17
sCI1-TS _{d4}	-5.79 (9.35)	-6.39	10.16
sCI1-TS _{d5}	-9.49 (8.25)	-10.08	5.99
sCI1-TS _{d6}	-10.20 (7.27)	-10.79	5.17
sCI1-TS _{d7}	-7.91 (9.56)	-8.51	7.30
sCI1-TS _{d8}	-10.70 (7.29)	-11.29	4.97
sCI1-P _d (ref. 1 and 3) + H ₂ O	-32.48	-32.48	-27.46
sCI1-P _d (ref. 2 and 4) + H ₂ O	-30.98	-30.98	-26.63
sCI1-P _d (ref. 5 and 7) + H ₂ O	-31.12	-31.12	-26.28
sCI1-P _d (ref. 6 and 8) + H ₂ O	-32.36	-32.35	-27.30

^a The values in parentheses are the activation barriers with respect to the corresponding reactant complexes.

-27.46 kcal mol $^{-1}$. Hence, the reaction of the sCI of β -pinene with $(\text{H}_2\text{O})_2$ is thermodynamically favorable. The reaction begins with the formation of a hydrogen-bonded reaction complex, RC by a barrierless reaction. The pre-reactive complexes of the sCI1 of β -pinene and $(\text{H}_2\text{O})_2$ are computed to lie 15.14–17.99 kcal mol $^{-1}$ below the energy of the reactants, which is lower than the complexes of the sCI1 of β -pinene and H₂O, which had binding energy values of -11.43 and -11.05 kcal mol $^{-1}$ at the M06-2X/6-311+G(2d,p) level. This result occurs because the pre-reactive complex of the sCI1 of β -pinene and $(\text{H}_2\text{O})_2$ contains one more water molecule, and therefore, more

hydrogen bond formation occurs, which makes the complex more stable than the complex of the sCI1 of β -pinene and H₂O. The activation barriers to the reaction of the sCI1 of β -pinene with $(\text{H}_2\text{O})_2$ (7.27–9.56 kcal mol $^{-1}$) are much lower than those of the reaction of the sCI1 of β -pinene with a single water molecule (12.21–16.58) relative to the energies of the corresponding hydrogen-bonded complexes. These results indicate that the reaction of the sCI with a water dimer is more favorable than the reaction of the sCI with a water monomer. Hence, we speculate that the reactions of the sCI of β -pinene with large water clusters may be even more energetically favorable. However, the number of water clusters in the atmosphere is rather low.⁷⁶ Therefore, the reactions of the sCI of β -pinene with large water clusters should be considered. There is also a need to study the chemistry of water clusters with large sCIs using theoretical, laboratory and atmospheric field measurements.

4. Conclusion

In this work, we have investigated the gas phase hydration reactions of the large biogenic sCIs from the ozonolysis of β -pinene, and the results reveal three important points.

(1) Comparing the structural parameters and the relative energies obtained with the B3LYP and M06-2X levels of theory, we found that the discrepancy between the results of the two functionals probably results from the description of the non-covalent interactions. To test the reliability of the B3LYP and M06-2X results, high-level single-point energy calculations were performed with the sCI1 of β -pinene and the monomer H₂O. Our results show that the binding energies, barrier heights and reaction energies calculated using the M06-2X functional are comparable with the values obtained with the DF-MP2/6-311++G(3df,2p) and CCSD(T)/6-31G(d) levels of theory. Therefore, the usage of M06-2X is advisable with reactions of the biogenic sCIs with water or water dimers.

(2) According to our calculations, the sCIs of β -pinene with the electron donor character of the cycloalkyl group have large energy barriers. Their position also plays an important role. The barrier of the reaction of the sCI1 of β -pinene (the *anti* configuration) with H₂O is larger than the barrier of the reaction of the sCI2 of β -pinene (the *syn* configuration) with H₂O, which can lead to the differences in the computations of the rate constants.

(3) The reactions of large biogenic sCIs with water dimers have lower activation energies than the reactions of the sCIs with water monomers. Hence, we speculate that the reaction of sCIs with larger water clusters will be even more energetically favorable, not considering the much lower concentrations of water clusters in the atmosphere. Therefore, the pathways of the reactions of sCIs with water clusters and especially with the water dimer should be considered.

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