

A theoretical study of the reactions of parent and substituted Criegee intermediates with water and the water dimer

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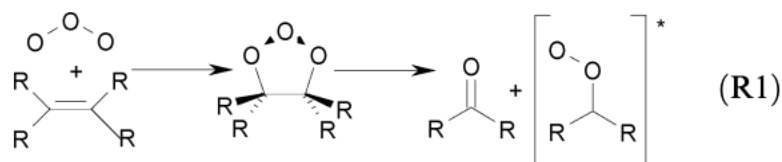
Abstract

A theoretical study was performed involving the reactions of a series of atmospherically significant Criegee intermediates (CIs), including parent, mono- and dimethyl - substituted CIs, with water and the water dimer at the CCSD(T)//B3LYP/6-311+G(2d,2p) level. We investigated two reaction routes leading to α -hydroxyalkyl hydroperoxide (HAHP). According to our calculations, the most favorable route is the formation of HAHP as the result of reactions of CIs with the water dimer. The rate constants for both pathways were calculated and the dependence of overall rate constant on temperature and relative humidity was also evaluated. The implication of our results to the chemistry of the troposphere is herein discussed.

Introduction

The ozone initiated oxidation of alkenes¹⁻³ is among the few reactions of closed shell molecules (non-radicals) leading to the formation of free radical species in the atmosphere. Ozonolysis reactions that were originally believed to be a sink for ozone in the atmosphere have attracted much attention as a source of key atmospheric oxidants such as HO_x and RO_x radicals and hydrogen- and organic peroxides.^{1,4-20} The former compounds were identified to cause damage to plants.²¹ The increased interest in ozonolysis originated in part from relatively high observed concentrations of alkenes in the troposphere from both natural and anthropogenic sources.²² Ozonolysis has thus been suggested to play a significant role in the atmospheric degradation of alkenes along with reactions initiated by HO, NO₃ or Cl radicals.²³ Another interesting aspect of ozonolysis reactions, besides the atmospheric chemistry, lies in the usage of ozone as a disinfectant for drinking water, where unsaturated hydrocarbons and their derivatives are identified contaminants.²⁴⁻²⁷ A detailed knowledge of kinetics and mechanism of the ozonolysis of alkenes is indeed fundamental in understanding the formation of reaction byproducts.

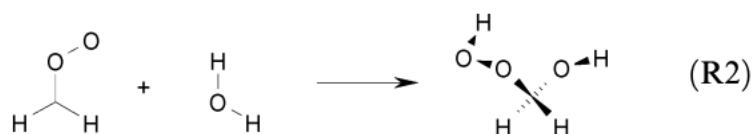
Originally, Criegee intermediate, often so-called carbonyl oxide, was postulated as intermediate in the ozonolysis reaction of alkenes in the liquid phase.²⁸ It was later shown that the same scenario is also applicable to the gas phase.^{29,30}



Reaction (R1) initially leads to the formation of a primary ozonide upon the ozone addition to the double bond. The ozonide subsequently undergoes cleavage at the C–C bond and one of the O–O bonds, leading to the formation of carbonyl compound and CI. Both are vibrationally excited, due

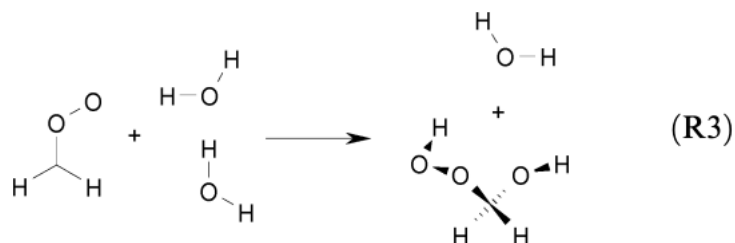
to excess energy generated by the high exothermicity of the ozonide decomposition reaction, *e.g.*, the reaction of ethene with ozone is exothermic by 49.2 kcal mol⁻¹.³¹ The fate of the CI is either unimolecular decomposition or collisional deactivation. The probability of the latter is about 40% for ethene,^{15,32–36} and varies from 3 to 40% for larger alkenes.^{17,29,34,36–38} under near atmospheric conditions. Recently measured stabilized CI yields for ethene, trans-2-butene, and 2,3-dimethyl-2-butene are 0.39, 0.24 and 0.10, respectively.³⁹ Deactivated CI is a very active and labile species, which reacts with various atmospheric compounds, such as HCHO, CH₃CHO, CO, NO, NO₂, SO₂ and H₂O.³⁰ The reaction with water is considered to be one of the most important secondary pathways for the CI consumption due to the high concentration of water vapor in the troposphere.

Hydroxymethyl hydroperoxide (HMHP),^{40,41} formic acid, aldehydes, ketones and H₂O₂^{4–7,20,42–44} have been experimentally observed among the products of the ozonolysis reaction of ethene in the presence of water. It has been proposed^{5,45} that HMHP is formed upon addition of water to the H₂COO:



This suggestion was supported later by a number of experimental studies. Becker *et al.*^{46,47} observed a good correlation between water vapor partial pressure and HMHP yield. Hatakeyama *et al.*⁴⁸ reported that the direct reaction of CH₂OO with H₂O is a source of HMHP, which was observed as the major peroxide formed in the gas phase in the presence of water vapor.⁴⁹ The yields of H₂O₂ and HMHP have been shown to increase up to 3–5 mbar water partial pressure, while decreasing if pressure is further increased.^{50,51} The yield of HMHP relative to O₃ consumption is 42% (C₂H₄), 14% (C₃H₆), 13% (*i*-C₄H₈) and 30% (isoprene) in the presence of 9000–18000 ppmv H₂O.⁷ Hasson *et al.*³⁹ have identified the products of the reaction of CIs with water to be entirely organic hydroperoxide or hydrogen peroxide, with a little acid formation. According to Monod *et al.*,⁵² the relatively high concentrations of HMHP in rain and cloud water⁵³ are explained by reactions of CIs at the droplet interface. The reaction of H₂COO with water was theoretically studied by Aplincourt *et al.*,⁵⁴ who found that this reaction proceeds *via* the formation of a hydrogen-bonded complex between reactants, with complexation energy of 7.2 kcal mol⁻¹ and activation energy of 9.5 kcal mol⁻¹. A later study by Crehuet *et al.*⁵⁵ at a higher theoretical level has resulted in complexation and activation energies 7.8 and 9.7 kcal mol⁻¹, respectively. Product of the reaction – HMHP can undergo subsequent reactions, which can lead to H₂O₂ formation.^{5,6,46,56,57} Different atmospheric observations show evidence that the H₂O₂ mixing ratio is strongly dependent on isoprene and ozone concentration.⁵⁸ Moortgat *et al.*⁵⁹ also discovered that H₂O₂ is formed from ozonolysis of alkenes together with its formation in an HO₂ recombination reaction in the atmosphere. Tremmel *et al.*^{60,61} observed a positive correlation between relative humidity and H₂O₂ levels in the troposphere.

The water dimer, which has been experimentally observed in the atmosphere⁶² can also react with CI. As mentioned by Vaida *et al.* in a recent review,⁶³ molecular clusters such as the water dimer can significantly affect the reactions of corresponding monomers. In our recent study,⁶⁴ we have suggested the novel additional channel for organic peroxide formation:



This pathway has lower activation barrier than the reaction of CI with one water molecule, and therefore can significantly influence the overall CI-water reaction despite the relatively low concentrations of water dimer.

In the present theoretical study, we investigated the reactions of parent, mono- and dimethylsubstituted Criegee intermediates with water and the water dimer, considering both reaction routes to provide deeper insight into the mechanism. We suggest that the most favorable route involves the reaction of CIs with the water dimer, leading to the formation of organic peroxides, namely hydroxylalkyl α -hydroperoxides (HAHP), which are also produced by the reaction of CIs with water. We also evaluated the reaction rate constants for these two pathways, and estimated the overall rate constant, as well as its dependence on temperature and relative humidity.

Computational details

All stationary points, molecules, complexes and transition states (TS), were obtained by geometry optimization using the hybrid density functional B3LYP method⁶⁵ with the 6-311+G(2d,2p)⁶⁶ basis sets. To verify the nature of the stationary points (either minima or saddle) the harmonic vibrational frequencies were calculated. They were also used to estimate zero-point vibration energy (ZPE) and the thermodynamic contribution to the enthalpy and free energy for $T = 298.15$ K. Additionally, intrinsic reaction coordinate calculations (IRC) were performed to examine the correspondence of the calculated TS to the reactants and products. Finally, single-point calculations at the CCSD and CCSD(T) level⁶⁷ using the same basis set were performed for B3LYP optimized structures geometries to obtain more accurate energy estimates. The basis set superposition error (BSSE) was calculated according to the function counterpoise method⁶⁸ at the CCSD and CCSD(T) levels of theory, which included the terms due to intramolecular deformation of the monomers in the complex geometry. All these calculations were performed using the Gaussian 98 program package.⁶⁹ The nature of bonding in complexes was analyzed using the AIM2000 program⁷⁰ based on atoms in molecules (AIM) theory.⁷¹ Reaction rate constants and equilibrium constants were estimated using conventional transition state theory (CTST),⁷² as implemented in the kinetics CSEO program suite⁷³ with CCSD(T) energies and Hessian obtained at the B3LYP level. Tunneling correction using the Eckart method was also applied.

Methods

We employed several quantum chemical methods to evaluate their effectiveness (quality and speed) in calculation of the energy barriers for the reactions of parent CI with water: MP2, CCSD(T)//MP2, B3LYP, CCSD//B3LYP, CCSD(T)//B3LYP, MP4(SDQ), MP4(SDQT)//MP4(SDQ), CCSD(T)//MP4(SDQ), QCISD, CCSD//QCISD, CCSD(T)/QCISD. The best available methods in Gaussian 98 applicable for geometry optimization (*i.e.*, which are provide analytical derivatives), QCISD and MP4(SDQ), were chosen as references. The detailed

results of this comparison study can be found in supplementary materials.[†] The second derivatives were calculated at the same level as the geometry optimization. CCSD(T) single point calculations based on geometry optimization by both reference methods gave almost the same results and the closest values to this level are demonstrated by energy calculations using the CCSD and CCSD(T) methods based on the B3LYP geometry optimization.

Results and discussion

All calculated relative reaction and activation energies, enthalpies, and free energies are shown in Tables 1 and 3. Reaction rate constants are depicted in Tables 2 and 4. We used the following designations to describe stationary structures in the text: **R** for reactants, **T** for transition states and **P** for products of reaction. The second character represents the Criegee intermediate: **p**, parent; **s**, *syn*-monomethyl; **a**, *anti*-monomethyl and **d**, dimethyl CI. The third character is used to represent number of water molecules participating in the reaction.

Table 1 Relative energies ΔE , relative enthalpies $\Delta H(298)$ and relative free energies $\Delta G(298)$ (kcal mol⁻¹) for optimized structures at B3LYP and CCSD(T) levels of theory using the 6-311+G(2d,2p) basis set for the formation of α -hydroxyalkyl hydroperoxide from the reaction of H₂COO, *syn*- and *anti*-HMeCOO, Me₂COO with H₂O

Structure	Relative to	B3LYP			CCSD(T), (BSSE)		
		ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
Rp1	H ₂ COO + H ₂ O	-6.8	-6.6	1.8	-7.4 (-5.8)	-7.2 (-5.6)	1.2 (2.8)
Tp1	Rp1	9.2	7.1	10.6	10.8	8.7	12.2
Pp1	Tp1	-40.9	-40.5	-41.3	-44.3	-43.9	-44.7
Rs1	<i>syn</i> -MeHCOO + H ₂ O	-7.3	-6.7	2.1	-9.2 (-7.5)	-7.7 (-6.0)	1.1 (2.8)
Ts1	Rs1	14.8	12.5	15.8	14.5	13.0	16.3
Ps1	Ts1	-39.3	-37.8	-38.6	-45.3	-42.1	-42.9
Ra1	<i>anti</i> -MeHCOO + H ₂ O	-8.1	-7.6	1.2	-10.6 (-8.8)	-9.0 (-8.2)	-0.2 (1.6)
Ta1	Ra1	9.4	7.1	10.3	9.4	7.8	11.1
Pa1	Ta1	-36.7	-35.3	-35.8	-43.4	-40.1	-40.6
Rd1	Me ₂ COO + H ₂ O	-7.4	-7.6	1.4	-10.5 (-8.6)	-8.9 (-6.8)	0.1 (2.0)
Td1	Rd1	14.4	13.2	16.3	14.5	12.4	15.5
Pd1	Td1	-33.7	-33.4	-33.7	-42.3	-38.9	-39.2

Table 2 Rate constants (k) and equilibrium constants (K_c) for the formation of α -hydroxyalkyl hydroperoxide from the reaction of H_2COO , *syn*- and *anti*- MeHCOO , and Me_2COO with H_2O computed by TST theory with Eckart tunneling correction, using energies calculated at CCSD(T) levels of theory with BSSE correction, 298 K and 101.325 kPa, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $\text{molecule}^{-1} \text{ cm}^3$

Reaction (\rightarrow)/Equilibrium (\rightleftharpoons)	k/K_c
$\text{H}_2\text{COO} + \text{H}_2\text{O} \rightarrow \text{Pp1}$	5.822×10^{-18}
$\text{Rp1} \rightarrow \text{Pp1}$	1.356×10^5
$\text{H}_2\text{COO} + \text{H}_2\text{O} \rightleftharpoons \text{Rp1}$	6.033×10^{-23}
$\text{H}_2\text{COO} + \text{H}_2\text{O} \rightleftharpoons \text{Rp1} \rightarrow \text{Pp1}$	8.181×10^{-18}
<i>syn</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightarrow \text{Ps1}$	7.329×10^{-21}
$\text{Rs1} \rightarrow \text{Ps1}$	5.867×10^2
<i>syn</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightleftharpoons \text{Rs1}$	1.997×10^{-23}
<i>syn</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightleftharpoons \text{Rs1} \rightarrow \text{Ps1}$	1.172×10^{-20}
<i>anti</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightarrow \text{Pa1}$	3.997×10^{-16}
$\text{Ra1} \rightarrow \text{Pa1}$	1.755×10^6
<i>anti</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightleftharpoons \text{Ra1}$	3.831×10^{-22}
<i>anti</i> - $\text{MeHCOO} + \text{H}_2\text{O} \rightleftharpoons \text{Ra1} \rightarrow \text{Pa1}$	6.723×10^{-16}
$\text{Me}_2\text{COO} + \text{H}_2\text{O} \rightarrow \text{Pd1}$	1.399×10^{-19}
$\text{Rd1} \rightarrow \text{Pd1}$	1.634×10^3
$\text{Me}_2\text{COO} + \text{H}_2\text{O} \rightleftharpoons \text{Rd1}$	1.774×10^{-22}
$\text{Me}_2\text{COO} + \text{H}_2\text{O} \rightleftharpoons \text{Rd1} \rightarrow \text{Pd1}$	2.899×10^{-19}

Table 3 Relative energies ΔE , relative enthalpies ΔH (298) and relative free energies ΔG (298) (kcal mol⁻¹) for optimized structures at B3LYP, CCSD and CCSD(T) levels of theory using the 6-311+G(2d,2p) basis set for reaction of CI with the water dimer

Structure	Relative to	B3LYP			CCSD, (BSSE)			CCSD(T), (BSSE)		
		ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
Rp2a	H ₂ COO + 2H ₂ O	-14.4	-14.9	4.2	-16.1	-16.5	2.5	-15.5	-16.0	3.1
Rp2b	H ₂ COO + 2H ₂ O	-14.5	-15.0	4.2	-16.3	-16.8	2.3	(-13.3)	(-13.8)	(4.3)
TP2a	Rp2a	3.7	1.2	4.6	7.8	5.3	8.7	-15.7	-16.2	2.9
TP2b	Rp2b	3.9	1.4	4.8	8.1	5.6	9.0	(-13.5)	(-14.0)	(5.1)
Pp2a	TP2a	-33.2	-32.4	-34.0	-41.7	-40.9	-42.5	6.6	4.1	7.5
Pp2b	TP2b	-33.7	-32.8	-34.5	-42.6	-41.7	-43.4	6.9	4.4	7.8
Pp2a	Pp1a + H ₂ O	-5.4	-6.1	3.7	-5.8	-6.5	-3.3	-38.4	-37.6	-39.2
Pp2b	Pp1b + H ₂ O	-5.9	-6.7	3.3	-6.7	-7.5	-2.4	-39.3	-38.4	-40.2
Rs2a	<i>syn</i> -MeHCOO + 2H ₂ O	-12.9	-13.8	4.2	-15.4	-16.4	1.7	-6.5	-7.3	-2.6
Rs2b	<i>syn</i> -MeHCOO + 2H ₂ O	-13.5	-14.5	3.7	(-14.4)	(-15.4)	(2.7)	-7.3	-8.0	-1.9
Ts2a	Rs2a	7.1	5.2	10.0	-16.2	-17.3	0.9	-15.3	-16.3	1.7
Ts2b	Rs2b	7.1	5.9	10.6	(-12.9)	(-13.0)	(5.2)	-16.1	-17.1	1.1
Ps2a	Ts2a	-30.0	-29.2	-31.0	10.8	9.0	13.8	9.4	7.5	12.3
Ps2b	Ts2b	-30.6	-29.7	-31.4	11.7	9.8	14.5	10.2	8.3	13.0
Ps2a	Ps1a + H ₂ O	-5.1	-5.8	4.0	-39.3	-38.5	-40.3	-35.9	-35.0	-36.8
Ps2b	Ps1b + H ₂ O	-6.1	-6.9	3.2	-40.2	-39.4	-41.1	-36.8	-36.0	-37.7
Ra2a	<i>anti</i> -MeHCOO + 2H ₂ O	-15.1	-16.3	2.0	-5.7	-6.4	-3.4	-6.4	-7.1	2.7
Ra2b	<i>anti</i> -MeHCOO + 2H ₂ O	-15.5	-16.7	1.9	-7.0	-7.8	-2.3	-7.7	-8.5	1.5
Ta2a	Ra2a	5.4	3.6	8.3	-17.6	-18.7	-0.5	-17.5	-18.7	-0.4
Ta2b	Ra2b	5.6	3.8	8.2	(-14.3)	(-15.4)	(2.8)	-18.0	-19.2	-0.6
Pa2a	Ta2a	-29.9	-29.1	-30.7	-18.0	-19.2	-0.6	-18.0	-19.2	-0.6
Pa2b	Ta2b	-30.4	-29.5	-31.2	(-14.6)	(-15.8)	(2.8)	-18.0	-19.2	-0.6
Pa2a	Pa1a + H ₂ O	-5.2	-5.9	3.9	9.2	7.4	12.1	7.4	5.6	10.3
Pa2b	Pa1b + H ₂ O	-5.8	-6.6	3.4	9.3	7.6	12.0	7.6	5.8	10.2
Rd2a	Me ₂ COO + 2H ₂ O	-14.9	-15.8	2.3	-28.5	-38.4	-40.0	-26.6	-35.1	-36.7
Rd2b	Me ₂ COO + 2H ₂ O	-15.3	-16.3	2.0	-40.3	-39.5	-41.2	-37.0	-36.2	-37.9
Td2a	Rd2a	10.8	8.9	14.0	-5.5	-6.2	-3.6	-6.2	-7.0	2.8
Td2b	Rd2b	10.9	9.1	14.0	-6.8	-7.5	-2.4	-7.5	-8.3	1.7
Pd2a	Td2a	-27.3	-26.5	-28.2	-17.7	-18.7	-0.5	-17.5	-18.7	-0.4
Pd2b	Td2b	-27.9	-27.2	-28.8	(-14.2)	(-15.2)	(3.0)	-18.0	-19.1	-0.2
Pd1a	Pd1a + H ₂ O	-27.3	-26.5	-28.2	(-14.6)	(-15.7)	(3.2)	-18.0	-19.1	-0.2
Pd1b	Pd1b + H ₂ O	-27.9	-27.2	-28.8	13.6	11.7	16.8	13.6	11.7	16.8
Pd2a	Pd1a + H ₂ O	-27.3	-26.5	-28.2	13.7	11.8	16.8	13.7	11.8	16.8
Pd2b	Pd1b + H ₂ O	-27.9	-27.2	-28.8	-37.5	-36.7	-38.4	-37.5	-36.7	-38.4
Pd1a	Pd1a + H ₂ O	-27.3	-26.5	-28.2	-38.6	-37.8	-39.5	-38.6	-37.8	-39.5
Pd1b	Pd1b + H ₂ O	-27.9	-27.2	-28.8	-5.6	-6.3	-3.5	-5.6	-6.3	-3.5
Pd2a	Pd1a + H ₂ O	-27.3	-26.5	-28.2	-7.1	-7.8	-2.2	-7.1	-7.8	-2.2
Pd2b	Pd1b + H ₂ O	-27.9	-27.2	-28.8	-7.1	-7.8	-2.2	-7.1	-7.8	-2.2

Table 4 Rate constants (k) and equilibrium constants (K_c) for the formation of α -hydroxyalkyl hydroperoxide from the reaction of CI with $(H_2O)_2$ computed by TST theory with Eckart tunneling correction, 298 K and 101.325 kPa, $cm^3 \text{ molecule}^{-1} s^{-1}$ and $\text{molecule}^{-1} cm^3$

Reaction (\rightarrow)/Equilibrium (\rightleftharpoons)	k/K_c
$H_2COO + (H_2O)_2 \rightarrow Pp2a$	1.135×10^{-12a}
$Rp2a \rightarrow Pp2a$	1.960×10^{10a}
$H_2COO + (H_2O)_2 \rightleftharpoons Rp2a$	7.466×10^{-23a}
$H_2COO + (H_2O)_2 \rightleftharpoons Rp2a \rightarrow Pp2a$	1.463×10^{-12a}
$H_2COO + (H_2O)_2 \rightarrow Pp2b$	8.887×10^{-13a}
$p2b \rightarrow Pp2b$	1.097×10^{10a}
$H_2COO + (H_2O)_2 \rightleftharpoons Rp2b$	1.075×10^{-22a}
$H_2COO + (H_2O)_2 \rightleftharpoons Rp2b \rightarrow Pp2b$	1.179×10^{-12a}
$Me_2COO + (H_2O)_2 \rightarrow Pd2a$	2.294×10^{-17c}
$Rd2a \rightarrow Pd2a$	8.533×10^{2c}
$Me_2COO + (H_2O)_2 \rightleftharpoons Rd2a$	7.600×10^{-20c}
$Me_2COO + (H_2O)_2 \rightleftharpoons Rd2a \rightarrow Pd2a$	6.485×10^{-17c}
$Me_2COO + (H_2O)_2 \rightarrow Pd2b$	3.481×10^{-17c}
$Rd2b \rightarrow Pd2b$	9.232×10^{2c}
$Me_2COO + (H_2O)_2 \rightleftharpoons Rd2b$	1.103×10^{-19c}
$Me_2COO + (H_2O)_2 \rightleftharpoons Rd2b \rightarrow Pd2b$	1.018×10^{-16c}
$syn\text{-}MeHCOO + (H_2O)_2 \rightarrow Ps2a$	6.359×10^{-16b}
$Rs2a \rightarrow Ps2a$	1.127×10^{4b}
$syn\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Rs2a$	1.021×10^{-19b}
$syn\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Rs2a \rightarrow Ps2a$	1.151×10^{-15b}
$syn\text{-}MeHCOO + (H_2O)_2 \rightarrow Ps2b$	5.597×10^{-16b}
$Rs2b \rightarrow Ps2b$	3.332×10^{3b}
$syn\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Rs2b$	3.097×10^{-19b}
$syn\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Rs2b \rightarrow Ps2b$	1.032×10^{-15b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightarrow Pa2a$	6.615×10^{-13b}
$Ra2a \rightarrow Pa2a$	2.131×10^{5b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Ra2a$	4.806×10^{-18b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Ra2a \rightarrow Pa2a$	1.024×10^{-12b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightarrow Pa2b$	1.385×10^{-12b}
$Ra2b \rightarrow Pa2b$	2.913×10^{5b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Ra2b$	9.509×10^{-18b}
$anti\text{-}MeHCOO + (H_2O)_2 \rightleftharpoons Ra2b \rightarrow Pa2b$	2.770×10^{-12b}

^a energy calculated at CCSD(T) levels of theory with BSSE correction. ^b energies calculated at CCSD(T) levels of theory. ^c energies calculated at B3LYP levels of theory with BSSE correction.

CI-water reaction

In previous theoretical studies,^{54,55,64,74} the reaction of H_2COO with water has been shown to proceed *via* the formation of the pre-reaction complex, **Rp1** (Fig. 1), leading to the production of HMHP (reaction 2). To properly address the nature of the complex we carried out AIM theory calculations. The values of bond critical points parameters satisfy criteria for hydrogen bonds^{75,76} and unambiguously characterize hydrogen type bonding between oxygen and hydrogen atoms in the complex (supplementary materials).[†] The accurate description of these kind of systems requires taking into account the BSSE estimation.^{77–79} We previously estimated the complexation energy for the $\text{H}_2\text{COO}\cdots\text{H}_2\text{O}$ complex is $7.4 \text{ kcal mol}^{-1}$ ($5.8 \text{ kcal mol}^{-1}$ after the BSSE correction),⁶⁴ which is slightly different from the corresponding values obtained by Anglada *et al.*⁵⁵ (8.8 and $7.8 \text{ kcal mol}^{-1}$, respectively). This difference is due to the fact that different levels of theory used for the ZPE calculation, and also since Anglada *et al.* used unperturbed geometry for the complex components for BSSE estimation. The corresponding complexes of monomethyl-substituted CI are slightly more stable, with bonding energy values of 9.2 and $10.6 \text{ kcal mol}^{-1}$ for *syn*- and *anti*-conformers (**Rs1** and **Ra1**, Fig. 1), respectively, while BSSE corrections lead to values of 7.5 and $8.8 \text{ kcal mol}^{-1}$ for these structures. The complexation energy of $\text{Me}_2\text{COO}\cdots\text{H}_2\text{O}$ (**Rd1**) is $10.5 \text{ kcal mol}^{-1}$ and $8.6 \text{ kcal mol}^{-1}$ after the BSSE correction. There are two types of $\text{CI}\cdots\text{H}_2\text{O}$ complexes. In the first type, an oxygen atom of water molecule forms a hydrogen bond with hydrogen atom connected to the central carbon atom of the CI (**Rp1** and **Ra1**). In the second type, hydrogen-bond is located between oxygen atom and hydrogen atom of methyl group (**Rs1** and **Rd1**). The latter is less stable. It is noteworthy that there is a direct dependence of the stabilization energy on number of methyl substitutes, which leads to the stabilization of the complex. **Ra1** and **Rd1** are more stable than **Rp1** and **Rs1**.

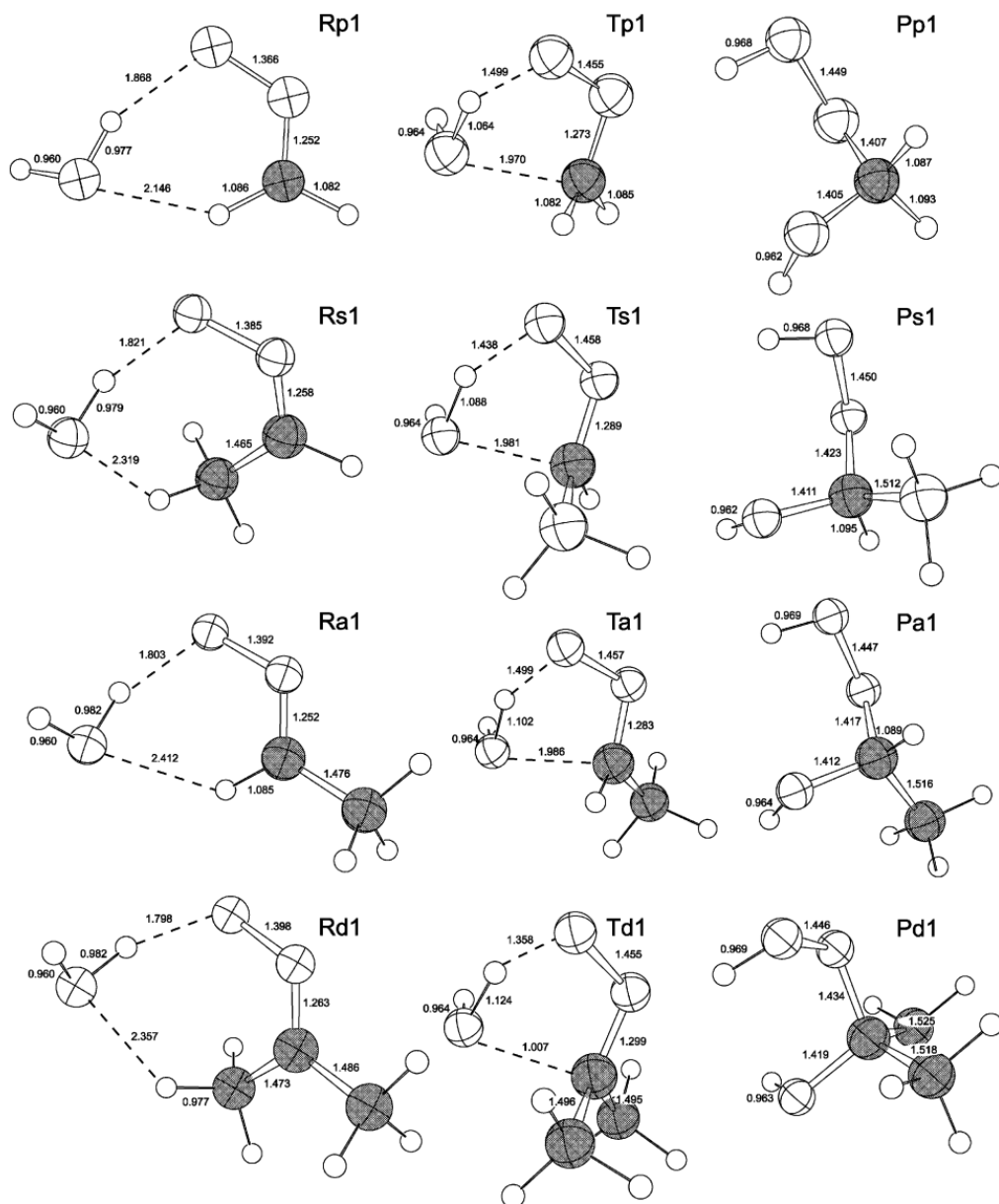


Fig. 1 Prereactive complexes, transition states and products of reactions $\text{RHC(=O)OH} + \text{H}_2\text{O} \rightarrow \text{RHC(OH)OOH}$, $\text{R} = \text{H}$ and Me .

The HAHF (**Pp1**, **Ps1**, **Pa1** and **Pd1**; Fig. 1) is formed through the cleavage of the H–O bond of the water molecule. In the transition states **Tp1**, **Ts1**, **Ta1** and **Td1** (Fig. 1), this bond was found to be slightly longer ($\text{R(HO)} = 1.064 \text{ \AA}$ for parent CI) than in the isolated water molecule ($\text{R(HO)} = 0.961 \text{ \AA}$). The hydrogen atom forms a bond with the terminal oxygen atom of carbonyl oxide while the HO fragment connects to the carbon atom of the carbonyl oxide (Fig. 1). The activation barriers for the reaction of *anti*-MeHCOO are slightly lower ($9.4 \text{ kcal mol}^{-1}$) than the parent CI ($10.8 \text{ kcal mol}^{-1}$). Reactions of *syn*-MeHCOO and Me_2COO appear to have higher activation energies ($14.5 \text{ kcal mol}^{-1}$; Table 1) due to the steric effects of the methyl groups, which are attached to the same side of CI as the terminal oxygen atom.

The rate constant for reaction of $\text{CI} + \text{H}_2\text{O}$ can be estimated in two different ways. In the first method, the formation of a reaction intermediate is ignored, for simplicity, and the reaction is

considered as an elementary reaction. In the second method, the reaction is considered as a two-step processes. In the first stage, a fast thermal equilibrium is established between the reactants and a complex. The second step includes the irreversible formation of peroxide. In the latter case, using the steady state approximation for the intermediate complex and an assumption of fast establishment of equilibrium between reactants, the overall rate constant is calculated as a product of the equilibrium constant of the complex formation and the rate constant for the second reaction step. Both approaches yield similar results with CTST theory without tunneling correction (Table 2). However, in order to take into account the tunneling effect, it is necessary to consider the reaction as a two-step process. Applying the BSSE correction to the energy of the complex does not change values of the overall calculated rate constants.

CI-water dimer reaction

In our previous study,⁴⁴ the reaction of H_2COO with the water dimer was found to have a lower activation energy than the reaction with a single water molecule. Here, we observe a similar effect for substituted CIs (Table 3, Figs. 2 and 3). The CI-water dimer pre-reaction complexes **Rp2**, **Rs2**, **Ra2** and **Rd2** were found to be 15.5 to 22.5 kcal mol⁻¹ more stable than the reactants. These values are approximately twice as large as the stabilization energies for the complexes with one water molecule (7.4–10.6 kcal mol⁻¹) (Tables 1 and 3). Figs. 2 and 3 illustrate that there are three bonds between carbonyl oxide and two molecules of water in CI-water dimer complexes, two hydrogen bonds and one “van der Waals”, which is supported through AIM theory calculations (see supplementary data).[†] One H-bond connects the terminal oxygen atom of carbonyl oxide to the hydrogen atom of first water molecule. The second H-bond links the two water molecules to each other. The third “Van der Waals” bond joins the oxygen atom of the second water molecule to the carbon atom of carbonyl oxide. As shown at Figs. 2 and 3, there are two forms of $\text{CI}-(\text{H}_2\text{O})_2$ complexes that are denoted as “a” and “b”, which have slightly different energy due to distinct orientations of the hydrogen atoms in the water molecules. The height of the activation barrier is dependent on the number of methyl groups of the CI complex. With an increase in substitution, the activation energy increases from 6.6 and 6.9 kcal mol⁻¹ (**Rp2a** and **Rp2b**) for the parent CI to 9.4, 10.2, 7.4 and 7.6 (**Ts2a**, **Ts2b**, **Ta2a** and **Ta2b**) kcal mol⁻¹ for monomethyl and to 13.6 and 13.7 kcal mol⁻¹ (**Td2a** and **Td2b**) for dimethyl-substituted compounds (Table 3).

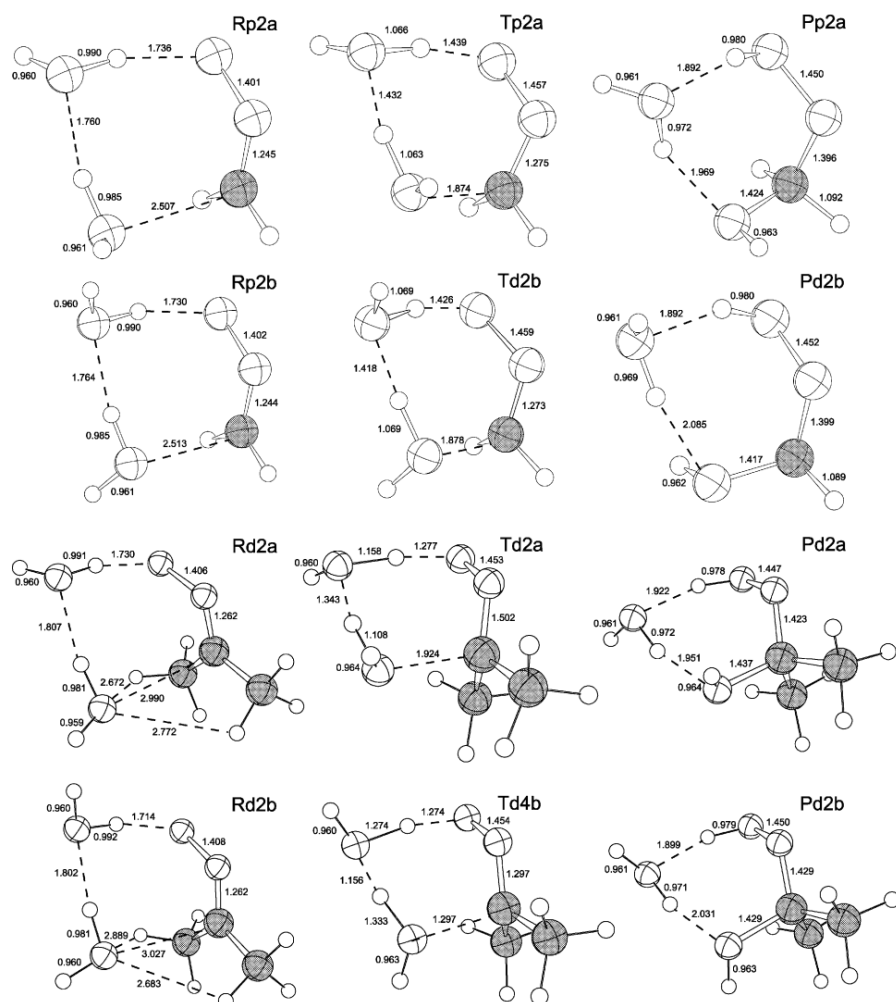


Fig. 2 Prereactive complexes, transition states and products of reactions $R_2COO + (H_2O)_2 \rightarrow R_2C(OH)OOH + H_2O$, $R = H$ and Me .

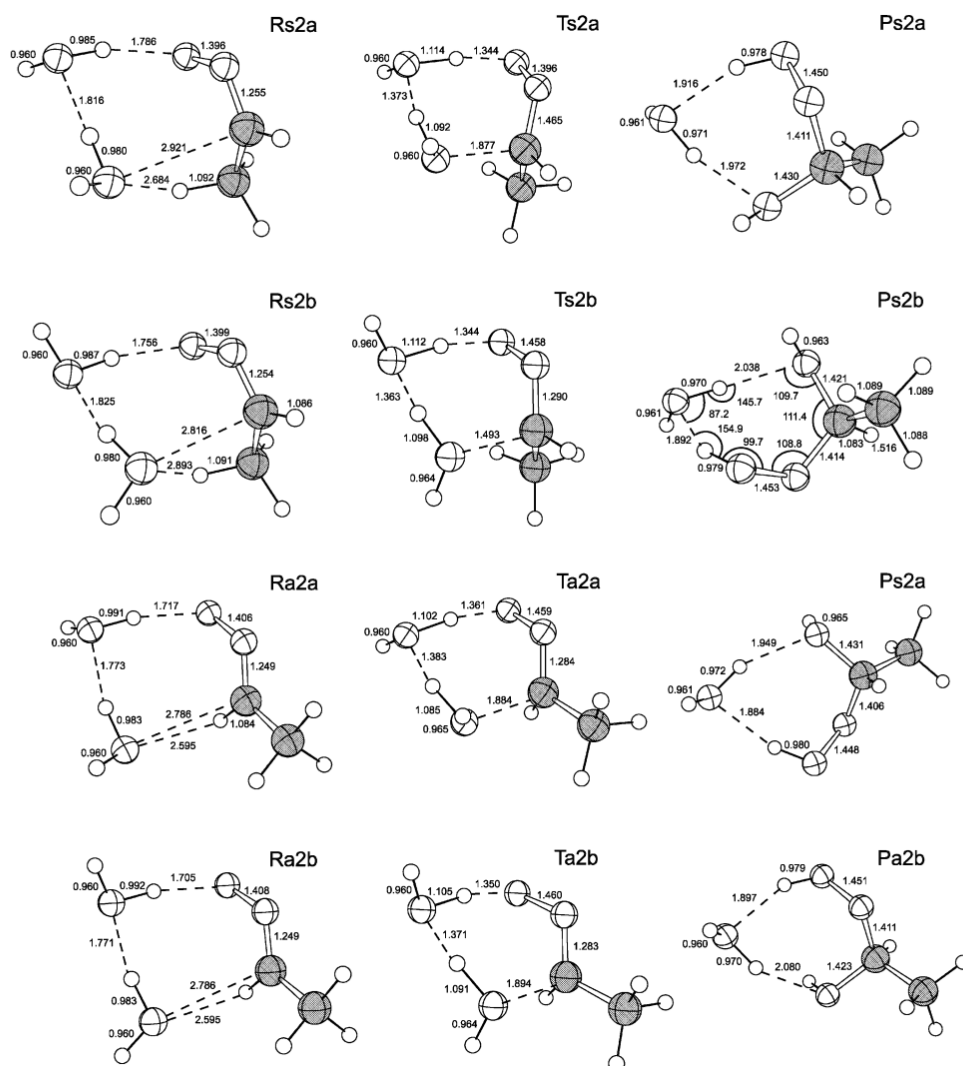


Fig. 3 Prereactive complexes, transition states and products of reactions $\text{MeHCOO} + (\text{H}_2\text{O})_2 \rightarrow \text{MeHC(OH)OOH} + \text{H}_2\text{O}$.

Our calculations demonstrate that the reaction of CI-water dimer complex leads to the formation of HAHP and a water molecule (reaction (3)). In the corresponding TS after cleavage of the H–O bond of the first water molecule, the hydrogen atom links to the terminal oxygen atom of carbonyl oxide, resulting in the formation of a peroxide. Simultaneously, the remaining fragment of the cleaved water molecule abstracts a hydrogen atom from the second water molecule to compensate for the loss of its hydrogen; this process can be considered as proton transfer. The HO fragment is thus formed upon separation of hydrogen from the second water molecule bonded to the carbon atom of carbonyl oxide. The products of the reaction can form hydrogen-bonded complexes **Pp2a**, **Pp2b**, **Ps2a**, **Ps2b**, **Pa2a**, **Pa2b**, **Pd2a** and **Pd2b** (Figs. 2 and 3), which have stabilization energies in a range 6.2–7.7 kcal mol^{−1} (Table 3). However, due to the large excess energy, these complexes are unlikely stable and undergo either decomposition or subsequent reactions that are discussed later on.

Rate constants $\text{CI} + (\text{H}_2\text{O})_2$ are calculated in two manners, similar to $\text{CI} + \text{H}_2\text{O}$ reactions that have already been described, they are listed in Table 4. The values of the rate constants are several

orders of magnitudes larger than the corresponding values for the reactions of CI with one water molecule. We examine the relative importance of water and water dimer routes, and the further fate of reaction products, in the next section of this paper.

Also four additional transition states were found for reaction of $\text{CI} + (\text{H}_2\text{O})_2$ with similar structure of TS of $\text{CI} + \text{H}_2\text{O}$ reaction, in which second water molecule attached by hydrogen bond to the first. Activation energies of these TS are very close to $\text{CI} + \text{H}_2\text{O}$ energy (8.0–12.1 vs. 9.2 kcal mol^{-1}). Therefore these reaction pathways are not significant due to much lower concentrations of water dimer. Energies and geometries of these calculated TS can be found in supplementary information.[†]

Atmospheric implications

Fig. 4 illustrates a comparison of the studied reaction routes for parent CI. Since the reaction intermediates have similar structures of reaction centres, the same trend in the reaction schemes is observed for all studied CIs (supplementary information).[†] According to our calculations, the most favorable pathway for the reaction of CI with water is the formation of HAHP. If we consider a second water molecule in this reaction, *i.e.*, CI interaction with water dimer, the activation barrier decreases significantly (Tables 1 and 3). It is thus quite reasonable to speculate that the reaction of CI with larger water clusters will be very energetically favorable, even considering the decrease in concentrations of water oligomers with the number of water molecules.⁸⁰ In analogy, one can consider the theoretical study of the self-reaction of HO_2 radicals in presence of water clusters⁸¹ in which reactions with water clusters appear to be more energetically favorable routes. Indeed, our recent results show that reactions of CI with water trimer have even lower values of activation energies than reaction with dimer.⁸² We thereafter encourage further theoretical, laboratory and atmospheric field measurements on the chemistry of water clusters with CI.

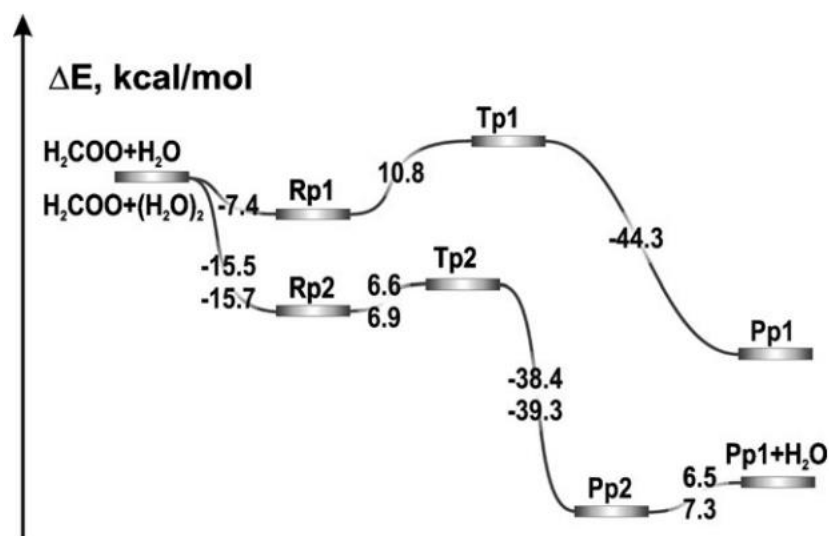


Fig. 4 Energy diagram for the reaction of H_2COO with H_2O and $(\text{H}_2\text{O})_2$.

Since the activation energy of the $\text{CI} + (\text{H}_2\text{O})_2$ reaction is significantly lower than that of the $\text{CI} + \text{H}_2\text{O}$ reaction, the rate constants should accordingly be significantly higher. However, the abundance of water dimers in atmosphere is rather low. Its concentration is estimated to be $\approx 0.2\%$ of total water under normal atmospheric conditions.⁸³ It is thus necessary to evaluate the reaction rates and compare them in order to evaluate the relative importance of the two calculated reaction routes. In this context, the following calculations were performed for a given parent CI. We

employed calculated values of standard enthalpy and entropy for the equilibria and Arrhenius parameters for the reaction rate constants (Table 5). Partial water pressure was determined as a product of relative humidity (RH) and saturation water vapor pressure, that was calculated according to the empirical Tetens formula:⁸⁴

$$p_s = 610.78 \exp(17.2694t)/(t + 238.3 \text{ K}) \quad (1)$$

where p_s is saturation water vapor pressure in Pascals and t is temperature in degrees Celsius. The partial pressure of water dimer was estimated using K_p obtained from Goldman *et al.*⁸⁵ Furthermore, the values of pressures were transformed to concentrations using the ideal gas law under standard pressure at given temperatures. Pseudo-first-order rate constants for the reactions were calculated by multiplying the concentrations of water and water dimer, by the rate constants of CI-water and CI water dimer reactions, correspondingly. For a wide range of RH and temperatures, the reaction with the water dimer proceeds faster than the reaction with the monomer, from about one order of magnitude faster at 303 K and 1% RH and to almost three orders of magnitude faster at 100% RH. The overall reaction can be assumed to be the sum of the three routes:

$$\begin{aligned} \frac{d[\text{H}_2\text{COO}]}{dt} = & -K_c(\mathbf{Rpl})k(\mathbf{Ppl})[\text{H}_2\text{COO}][\text{H}_2\text{O}] \\ & - \{K_c(\mathbf{Rp2a})k(\mathbf{Pp2a}) + K_c(\mathbf{Rp2b})k(\mathbf{Pp2b})\} \\ & \times [\text{H}_2\text{COO}][(\text{H}_2\text{O})_2] \end{aligned} \quad (2)$$

The concentration of water dimer can be found through constant $K_c((\text{H}_2\text{O})_2)$ of the equilibrium $2\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2$, and then substituted in eqn. (2):

$$\begin{aligned} \frac{d[\text{H}_2\text{COO}]}{dt} = & -K_c(\mathbf{Rpl})k(\mathbf{Ppl})[\text{H}_2\text{COO}][\text{H}_2\text{O}] \\ & - \{K_c(\mathbf{Rp2a})k(\mathbf{Pp2a}) + K_c(\mathbf{Rp2b})k(\mathbf{Pp2b})\} \\ & \times [\text{H}_2\text{COO}]K_c((\text{H}_2\text{O})_2)[\text{H}_2\text{O}]^2 \end{aligned} \quad (3)$$

This expression can be divided by the water and CI concentrations to obtain the observed second-order rate constant:

$$\begin{aligned} k_{\text{obs}} = & K_c(\mathbf{Rpl})k(\mathbf{Ppl}) + \{K_c(\mathbf{Rp2a})k(\mathbf{Pp2a}) \\ & + K_c(\mathbf{Rp2b})\}k(\mathbf{Rp2b})\}K_c((\text{H}_2\text{O})_2)[\text{H}_2\text{O}] \end{aligned} \quad (4)$$

The observed rate constant is temperature dependent. The complex reaction consists of four equilibria and three elementary reactions, which are in turn temperature dependent. There is also a linear dependence of k_{obs} on water concentration, that is itself linearly dependent on RH and nonlinearly on temperature. Fig. 5 illustrates a large variation in the rate constants (\sim two orders of magnitude – from 7.4×10^{-17} to $1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with RH and temperature.

Unfortunately, the $\text{CI} + \text{H}_2\text{O}$ reaction have not been directly studied in gas phase so far and only relative rate constants are available. As result, these kinetic data are inconsistent and differ by several orders of magnitude^{30,86,87} ranging from 1×10^{-19} to $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Only one study of the absolute rate constant of $\text{CI} + \text{H}_2\text{O}$ reaction is known to the authors, namely the liquid phase reaction of diphenyl CI with water in the MeCN medium,⁸⁸ which is $4.7 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($7.8 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Nevertheless, obtained in this work values of the rate constant of $\text{H}_2\text{COO} + \text{H}_2\text{O}$ reaction agrees with previous experimental studies and fall into the range of experimentally found constants. The established dependence of this constant on temperature and relative humidity can particularly explain the large variety of the experimentally obtained rate constants.

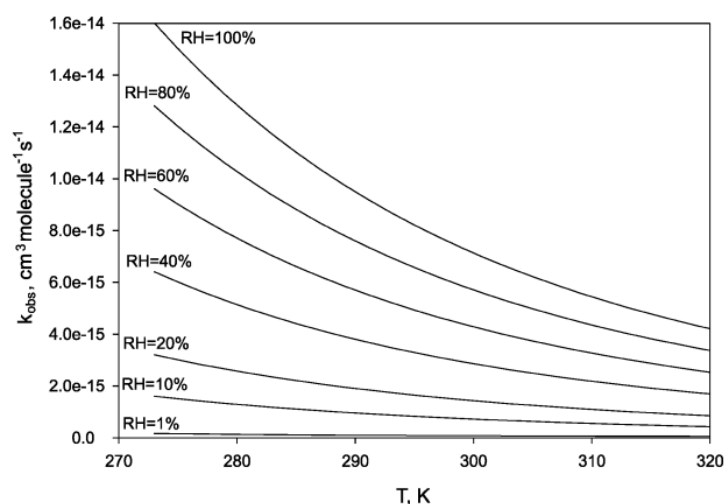


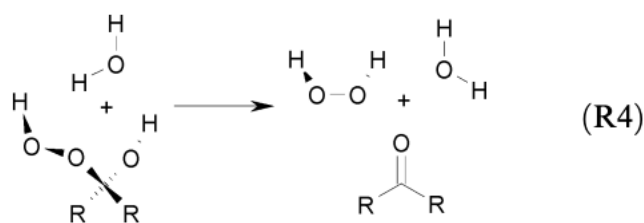
Fig. 5 Dependence of observed rate constant of the $\text{H}_2\text{COO} + \text{H}_2\text{O}$ reaction on temperature and relative humidity (RH).

Table 5 Parameters for reactions of the parent CI with water and water dimer, obtained using energies calculated at CCSD(T)//B3LYP/6-311+(2p,2d) level with BSSE correction and Hessian calculated at B3LYP/6-311+(2p,2d) level with tunneling correction

Equilibrium	$\Delta H_{298}^\circ / \text{kcal mol}^{-1}$	$\Delta S_{298}^\circ / \text{cal mol}^{-1} \text{ K}^{-1}$
$\text{H}_2\text{COO} + \text{H}_2\text{O} \rightleftharpoons \text{Rp1}$	-5.586	-31.692
$\text{H}_2\text{COO} + (\text{H}_2\text{O})_2 \rightleftharpoons \text{Rp2a}$	-9.397	-44.058
$\text{H}_2\text{COO} + (\text{H}_2\text{O})_2 \rightleftharpoons \text{Rp2b}$	-9.599	-44.011
Reaction	Arrhenius equation ^a for $k(T)$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
Rp1 \rightarrow Pp1	$k(T) = 1.43775 \times 10^{10} (T^{0.18101}) \exp(-3.75754 \times 10^3/T)$	
Rp2a \rightarrow Pp2a	$k(T) = 6.48724 \times 10^9 (T^{0.34526}) \exp(-2.58158 \times 10^2/T)$	
Rp2b \rightarrow Pp2b	$k(T) = 3.21288 \times 10^9 (T^{0.42406}) \exp(-3.55692 \times 10^2/T)$	

^a $T = 250\text{--}350 \text{ K}$.

Another interesting result following from the calculations is that the products of the reaction of CI with water dimer are HAHP and water. The former can undergo further transformations. According to theoretical studies,^{55,74} the most energetically favourable channel of HAHP is decomposition to OH and hydroxyalkoxy (R_2COOH) radicals. However the recent experimental works^{39,89} indicate that this decomposition pathway may not be significant. The other possibilities for the HAHP reaction are decomposition to either (a) an acid molecule and water (with activation energies $E_a = 49.2$ – 52.7 and 49.3 kcal mol⁻¹ for parent and monomethyl CIs respectively), or (b) a carbonyl compound and hydrogen peroxide ($E_a = 52.0$, 48.6 , 51.3 kcal mol⁻¹ for parent, monomethyl and dimethyl CIs).^{55,74} The same processes can occur with the participation of water molecule, which acts like a catalyst. In this case, the activation barriers are significantly lower: $E_a = 38.3$ – 40.4 , 34.4 – 38.1 kcal mol⁻¹ for the formation of acid, and $E_a = 25.6$, 26.2 , 25.5 kcal mol⁻¹ for the formation of H_2O_2 . If we consider that the reaction of CI with water dimer yields HAHP and a water molecule or HAHP-water complex, we can speculate that HAHP can react with this water molecule to further produce hydrogen peroxide, along with corresponding aldehyde or ketone. The excess energy in the HAHP formation process is enough (38.4 – 39.3 , 29.5 – 40.8 and 28.1 – 41.8 kcal mol⁻¹ accordingly for parent, mono and dimethyl CIs) to favor conformation changes and to overcome the activation barrier of the reaction:



This is also supported by fact that HMHP very easily dissociates in aqueous solution giving H_2O_2 .⁹⁰⁻⁹³

Concluding remarks

Two reaction routes for substituted Criegee intermediates with water and water the dimer were studied. The predominant pathway under the atmospheric conditions is found to be the reaction with the water dimer. We hence confirm that hydrogen peroxide in the atmosphere can indeed be produced in addition to well-characterized self-reactions of HO_2 radicals,² through secondary reactions of HAHP with water and water dimer.

The relative energies obtained at the CCSD and CCSD(T) levels of theory usually differ from the B3LYP energies by 0–6 kcal mol⁻¹, with occasional difference of 6.7–14.5 kcal mol⁻¹. Therefore, the usage of the CCSD or CCSD(T) methods for energy calculations is advisable for reactions such as CI with water and water dimers. The difference between CCSD and CCSD(T) energies is small, usually a few kcal mol⁻¹ (ranging from 0.1 to 3.4 kcal mol⁻¹). The usage of CCSD single point calculations is thus justified when the calculations at CCSD(T) level are not possible.

Acknowledgements

The Centre for Climate and Global Change Research (C²GCR), McGill University, the Natural Sciences and Engineering Research Council in Canada (NSERC), the Canada Foundation for Innovation (CFI) and Le Fonds Québécois de Recherche sur la Nature et les Technologies for funding this research. The Centre for Research in Molecular Modeling (CERMM), Concordia University for computational resources. Dr N. Goldman for communicating with us his calculation of the equilibrium constants of water dimer formation. Prof. J. M. Anglada for discussing with us

his recent publications. Drs Q. Timerghazin and A. Khalizov for valuable suggestions. E. Hudson and J. Johnstone for proofreading this manuscript.

References

1. S. E. Paulson and J. J. Orlando, *Geophys. Res. Lett.*, 1996, **23**, 3727.
2. P. A. Ariya, R. Sander and P. J. Crutzen, *J. Geophys. Res., (Atmos.)*, 2000, **105**, 17721.
3. M. Lee, B. G. Heikes and D. W. O'Sullivan, *Atmos. Environ.*, 2000, **34**, 3475.
4. R. I. Martinez, J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, 1981, **103**, 3807.
5. S. Gaeb, E. Hellpointner, W. V. Turner and F. Kortem, *Nature*, 1985, **316**, 535.
6. K. H. Becker, K. J. Brockmann and J. Bechara, *Nature*, 1990, **346**, 256.
7. P. Neeb, F. Sauer, O. Horie and G. K. Moortgat, *Atmos. Environ.*, 1997, **31**, 1417.
8. F. Sauer, C. Schafer, P. Neeb, O. Horie and G. K. Moortgat, *Atmos. Environ.*, 1999, **33**, 229.
9. R. Atkinson, S. M. Aschmann, J. Arey and B. Shorees, *J. Geophys. Res., (Atmos.)*, 1992, **97**, 6065.
10. R. Atkinson and S. M. Aschmann, *Environ. Sci. Technol.*, 1993, **27**, 1357.
11. R. Atkinson, E. C. Tuazon and S. M. Aschmann, *Environ. Sci. Technol.*, 1995, **29**, 1860.
12. S. E. Paulson, A. D. Sen, P. Liu, J. D. Fenske and M. J. Fox, *Geophys. Res. Lett.*, 1997, **24**, 3193.
13. S. E. Paulson, *Adv. Ser. Phys. Chem.*, 1995, **3**, 111.
14. S. E. Paulson, M. Y. Chung and A. S. Hasson, *J. Phys. Chem. A*, 1999, **103**, 8125.
15. H. Niki, P. D. Maker, C. M. Savage and L. P. J. Breitenbach, *Phys. Chem.*, 1981, **85**, 1024.
16. P. Neeb, O. Horie, S. Limbach and G. K. Moortgat, *Transp. Transform. Pollut. Troposphere, Proc. EUROTRAC Symp., 3rd*, 1994, 128.
17. A. S. Hasson, A. W. Ho, K. T. Kuwata and S. E. Paulson, *J. Geophys. Res., (Atmos.)*, 2001, **106**, 34143.
18. J. H. Kroll, J. S. Clarke, N. M. Donahue, J. G. Anderson and K. L. Demerjian, *J. Phys. Chem. A*, 2001, **105**, 1554.
19. J. H. Kroll, S. R. Sahay, J. G. Anderson, K. L. Demerjian and N. M. Donahue, *J. Phys. Chem. A*, 2001, **105**, 4446.
20. S. Wolff, A. Boddenberg, J. Thamm, W. V. Turner and S. Gab, *Atmos. Environ.*, 1997, **31**, 2965.
21. C. N. Hewitt, G. L. Kok and R. Fall, *Nature*, 1990, **344**, 56.
22. M. T. Benjamin, M. Sudol, L. Bloch and A. M. Winer, *Atmos. Environ.*, 1996, **30**, 1437.
23. R. Atkinson, *Atmos. Environ.*, 2000, **34**, 2063.
24. J. Hoigne and H. Bader, *Water Res.*, 1983, **17**, 173.
25. S. D. Richardson, A. D. Thruston, Jr., T. V. Caughran, P. H. Chen, T. W. Collette, K. M. Schenck, B. W. Lykins, Jr., C. Rav-Acha and V. Glezer, *Water Air Soil Pollut.*, 2000, **123**, 95.
26. C. A. Fronk, *Ozone: Sci. Eng.*, 1987, **9**, 265.
27. P. Dowd and C. von Sonntag, *Environ. Sci. Technol.*, 1998, **32**, 1112.
28. R. Criegee and G. Wenner, *Ann.*, 1949, **564**, 9.
29. H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *Chem. Phys. Lett.*, 1977, **46**, 327.
30. S. Hatakeyama and H. Akimoto, *Res. Chem. Intermed.*, 1994, **20**, 503.
31. J. M. Anglada, R. Crehuet and J. Maria Bofill, *Chem.-Eur. J.*, 1999, **5**, 1809.
32. F. Su, J. G. Calvert and J. H. Shaw, *J. Phys. Chem.*, 1980, **84**, 239.
33. C. S. Kan, F. Su, J. G. Calvert and J. H. Shaw, *J. Phys. Chem.*, 1981, **85**, 2359.
34. S. Hatakeyama, H. Kobayashi and H. Akimoto, *J. Phys. Chem.*, 1984, **88**, 4736.
35. S. Hatakeyama, H. Kobayashi, Z. Y. Lin, H. Takagi and H. Akimoto, *J. Phys. Chem.*, 1986, **90**, 4131.
36. O. Horie and G. K. Moortgat, *Atmos. Environ., Part A*, 1991, **25A**, 1881.
37. O. Horie, P. Neeb and G. K. Moortgat, *Int. J. Chem. Kinet.*, 1997, **29**, 461.
38. S. E. Paulson and J. H. Seinfeld, *Environ. Sci. Technol.*, 1992, **26**, 1165.
39. A. S. Hasson, G. Orzechowska and S. E. Paulson, *J. Geophys. Res., (Atmos.)*, 2001, **106**, 34131.
40. A. Rieche and R. Meister, *Ber.*, 1935, **68B**, 1465.
41. A. V. Karyakin and V. A. Nikitin, *Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya*, 1953, **17**, 636.
42. F. Sauer, C. Schafer, P. Neeb, O. Horie and G. K. Moortgat, *Atmos. Environ.*, 1998, **33**, 229.
43. C. N. Hewitt and G. L. Kok, *J. Atmos. Chem.*, 1991, **12**, 181.
44. S. Wolff, W. V. Turner, S. Gaeb, S. Moenninghoff, L. Ruppert and K. Brockmann, *Transp. Chem. Transform. Pollut. Troposphere*, 1997, **3**, 106.
45. S. Hatakeyama, H. Bandow, M. Okuda and H. Akimoto, *J. Phys. Chem.*, 1981, **85**, 2249.
46. K. H. Becker, J. Bechara and K. Brockmann, *J. Atmos. Environ., Part A*, 1993, **27A**, 57.
47. K. H. Becker, H. Plagens, "Optimization of the sampling of hydroperoxides and studies of the water vapor dependence of the hydroperoxide formation in ozonolysis of alkenes," Fachbereich 9 Physikalische Chemie, Gesamthochschule Wuppertal, Wuppertal, Germany, 1997.
48. S. Hatakeyama, H. Lai, S. Gao and K. Murano, *Chem. Lett.*, 1993, 1287.
49. O. Horie, P. Neeb, S. Limbach and G. K. Moortgat, *Geophys. Res. Lett.*, 1994, **21**, 1523.
50. K. H. Becker, S. Moenninghoff, "Formation of hydroperoxides in the ozonolysis of ethene in presence of water vapor," Fachbereich 9 Physikalische Chemie, Bergische Univ. Gesamthochschule Wuppertal, Wuppertal, Germany. FIELD URL., 1998.
51. K. J. Brockmann, S. Monninghoff, L. Ruppert, "The Formation of Peroxides, in The European Photoreactor EUPHORE: Design and Technical Development of the European Photoreactor and First Experimental Results Final report of the EC project Contract EV5V-CT92-0059, edited by K. H. Becker", 1996.
52. A. Monod, A. Chebbi, R. Durand-Jolibois and P. Carlier, *Atmos. Environ.*, 2000, **34**, 5283.
53. F. Sauer, C. Schuster, C. Schafer and G. K. Moortgat, *Geophys. Res. Lett.*, 1996, **23**, 2605.
54. P. Aplincourt and M. F. Ruiz-Lopez, *J. Am. Chem. Soc.*, 2000, **122**, 8990.
55. R. Crehuet, J. M. Anglada and J. M. Bofill, *Chem.-Eur. J.*, 2001, **7**, 2227.

56. R. Simonaitis, K. J. Olszyna and J. F. Meagher, *Geophys. Res. Lett.*, 1991, **18**, 9.
57. S. Gaeb, W. V. Turner, S. Wolff, K. H. Becker, L. Ruppert and K. J. Brockmann, *Atmos. Environ.*, 1995, **29**, 2401.
58. F. Sauer, J. Beck, G. Schuster and G. K. Moortgat, *Chemosphere*, 2001, **3**, 309.
59. G. K. Moortgat, D. Grossmann, A. Boddenberg, G. Dallmann, A. P. Ligon, W. V. Turner, S. Gaeb, F. Slemr, W. Wieprecht, K. Acker, M. Kibler, S. Schlomski and K. Baechmann, *J. Atmos. Chem.*, 2002, **42**, 443.
60. H. G. Tremmel, W. Junkermann, F. Slemr and U. Platt, *J. Geophys. Res.*, (Atmos.), 1993, **98**, 1083.
61. H. G. Tremmel, W. Junkermann and F. Slemr, *European Commission, (Report) EUR*, 1994, p. 238.
62. K. Pfeilsticker, A. Lotter, C. Peters and H. Boesch, *Science*, 2003, **300**, 2078.
63. V. Vaida, H. G. Kjaergaard and K. Feierabend, *Int. Rev. Phys. Chem.*, 2003, **22**, 203.
64. A. B. Ryzhkov and P. A. Ariya, *Chem. Phys. Lett.*, 2002, **367**, 423.
65. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
66. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
67. K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479.
68. P. Valiron and I. Mayer, *Chem. Phys. Lett.*, 1997, **275**, 46.
69. M. J. Frisch, *et al.*, *GAUSSIAN 98, (Revision A.7)*, Gaussian Inc., Pittsburgh, PA, 1998.
70. F. B. König, J. Schonbohm and D. Bayles, *J. Comput. Chem.*, 2001, **22**, 545.
71. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1994.
72. W. T. Duncan, R. L. Bell and T. N. Truong, *J. Comput. Chem.*, 1998, **19**, 1039.
73. S. Zhang and T. N. Truong, *Kinetics (CSEO version 1.0)*, University of Utah, 2003.
74. J. M. Anglada, P. Aplincourt, J. M. Bofill and D. Cremer, *ChemPhysChem*, 2002, **3**, 215.
75. U. Koch and P. L. A. Popelier, *J. Phys. Chem.*, 1995, **99**, 9747.
76. P. L. A. Popelier, *J. Phys. Chem. A*, 1998, **102**, 1873.
77. J. J. Novoa, M. Planas and M. C. Rovira, *Chem. Phys. Lett.*, 1996, **251**, 33.
78. S. Simon, J. Bertran and M. Sodupe, *J. Phys. Chem. A*, 2001, **105**, 4359.
79. A. Bende, M. Knapp-Mohammady and S. Suhai, *Int. J. Quantum Chem.*, 2003, **92**, 152.
80. G. T. Evans and V. Vaida, *J. Chem. Phys.*, 2000, **113**, 6652.
81. R. S. Zhu and M. C. Lin, *PhysChemComm*, 2003, 51.
82. A. B. Ryzhkov and P. Ariya, *Abstracts of Papers, Annual APS Meeting*, Montreal, Canada, March 22–26, 2004.
83. N. Goldman, R. S. Fellers, C. Leforestier and R. J. Saykally, *J. Phys. Chem. A*, 2001, **105**, 515.
84. F. W. Murray, *J. Appl. Meteorol.*, 1967, **6**, 203.
85. N. Goldman, C. Leforestier and R. J. Saykally, *J. Phys. Chem. A*, 2004, **108**(5), 787–794.
86. D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, J. Troe and R. T. Watson, *J. Phys. Chem. Ref. Data*, 1980, **9**, 295.
87. J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington and G. Yarwood, *The Mechanisms of Atmospheric Oxidation of the Alkenes*, 1999.
88. A. M. Nazarov, S. L. Khursan, I. A. Kalinichenko, S. K. Ziganshina and V. D. Komissarov, *Kinet. Catal. (Transl. Kinet. Katal.)*, 2002, **43**, 459.
89. A. S. Hasson, M. Y. Chung, K. T. Kuwata, A. D. Converse, D. Krohn and S. E. Paulson, *J. Phys. Chem. A*, 2003, **107**, 6176.
90. S. Marklund, *Acta Chem. Scand.*, 1971, **25**, 3517.
91. E. Bothe and D. Schulte-Frohlinde, *Z. Naturforsch. B*, 1980, **35B**, 1035.
92. X. Zhou and Y. N. Lee, *J. Phys. Chem.*, 1992, **96**, 265.
93. E. Chevallier, R. D. Jolibois, B. Picquet, P. Carlier, S. Francois and A. Monod, “Tropospheric Reactivity of Organic Hydroperoxides”; 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 2001, Torino.