Probing Criegee intermediate reactions with methanol by FTMW spectroscopy†

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Criegee intermediates (CIs) are carbonyl oxides generated from ozonolysis of unsaturated hydrocarbons in the atmosphere. The relatively long lifetime of CIs makes possible the bimolecular reactions with other atmospheric agents. These reactions can potentially be fast enough to contribute significantly to the tropospheric budgets of those species or to alter the rate of generation of secondary organic aerosols (SOAs). In particular, the new adducts formed in these reactions contribute SOA formation because they have larger molecular weights and lower vapor pressures than the reactants and are more condensable. α -alkoxyalkyl hydroperoxides are the nascent products derived from the insertion reactions of CIs with alcohols. In this work we report the direct detection of methoxymethyl hydroperoxide (HOOCH₂OCH₃, MMHP) and methoxyethyl hydroperoxide (HOO(CH₂)HOCH₃, MEHP) as the reaction products between the CIs, CH₂OO and CH₃CHOO and methanol. High resolution Fourier transform microwave spectroscopy has been used to identify one and two conformers of MMHP and MEHP, respectively. The pre-reactive complex CH₂OO–CH₃OH was not observed in this experiment, which indicates that CH₂OO shows a different reactivity toward methanol than that toward water. Our results for CH₃CHOO + CH₃OH show that MEHP is produced in similar ratios when *syn*- and *anti*-CH₃CHOO react with methanol vapor.

Introduction

Criegee intermediates (CIs) are reactive species formed in the ozonolysis of alkenes.¹ Their formation is attributed to ring-opening of primary ozonides (POZs) formed directly by the 1,3-cycloaddition reaction of ozone across the olefinic bond. Nascent CIs possess a range of internal energies, a varying proportion of which possess sufficient excitation for prompt decomposition. The remainder of CIs collisionally stabilized, named stabilized Criegee intermediates (SCIs), will be sufficiently long-lived with respect to unimolecular processes that they may also engage in bimolecular reactions with several atmospheric species. Hence, the subsequent chemistry of SCIs is related to the atmospheric cycles of species such as NO_x and HO_x or to the secondary organic aerosols (SOAs), which are formed by their reaction towards H₂O,^{2–4} SO₂^{5–7} or carboxylic acids.^{8,9}

Alcohols are a prevalent class of oxygenated volatile organic compounds (OVOCs) in the atmosphere and have terrestrial biogenic sources of which tropical rainforests are among the largest.¹⁰ Methanol is the most abundant alcohol in the troposphere.^{11,12} In fact it is the most abundant organic compound after methane.^{13–15} Because of the high flux of SCIs, co-location is expected between methanol and SCIs in the troposphere, and then reactions involving both species could have important atmospheric implications. These CIs with methanol is known to produce α -methoxyalkyl hydroperoxides¹⁶ (MAHPs, Scheme 1) in a reaction that can be viewed as an effective insertion of the carbonyl oxide into the O–H bond, similar to the reaction between CIs with water. MAHPs are a potential source of OH radicals and may be significant in terms of the SOAs formation in the troposphere.^{17–19}

Just in the last three years, several works have been devoted to investigate the reactions between CIs and alcohols, especially

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Scheme 1 Formation of MAHPs from Criegee intermediates.

those with methanol. McGillen *et al.*¹⁹ reported the rate coefficients for the reactions of CH_2OO and $(\text{CH}_3)_2\text{COO}$ with methanol and that of CH_2OO with ethanol, and found that substitution on the Criegee intermediate has a strong influence over the reaction rate, whereas substitution on the alcohol moiety does not. Similar conclusion was reached by Tadayon *et al.*²⁰ who investigated the reactions between CH_2OO and methanol, ethanol, and 2-propanol. More recently the reactivity of the singly methyl substituted CI, CH_3CHOO , towards methanol has been investigated by Lin *et al.*²¹ and Chao *et al.*²² These authors found that the reaction of *syn*- CH_3CHOO with methanol is enhanced by a single water molecule under ambient conditions. In addition, they observed a competing channel of *syn*- $\text{CH}_3\text{CHOO} + 2\text{CH}_3\text{OH}$ and evaluated the kinetic isotopic effects for the reactions. Alcohol-CI reactions have also been explored using quantum chemical calculations. Aroeira *et al.*²³ studied the reactions of CH_2OO and $(\text{CH}_3)_2\text{COO}$ with methanol employing rigorous *ab initio* methods while Watson *et al.*²⁴ have performed the most comprehensive computational study of alcohol-CI reactions including up to 22 different CIs.

In this paper we describe a combined experimental and computational study of the reactions between the simplest CI, CH_2OO , and its methyl derivative, CH_3CHOO , towards methanol. The nascent products resulting from these two reactions have been characterized using high resolution Fourier transform microwave spectroscopy in combination with electric discharges. Complementary high level *ab initio* calculations have been performed to map out the reaction pathways and to identify the nature of the reaction products. The reactivity trend of each CH_3CHOO conformer is derived from the intensity of their rotational spectra, and it is compared to previously reported results.

Quantum chemical calculations

Quantum chemical calculations on the reactions of CH_2OO and CH_3CHOO with CH_3OH have been reported previously.^{19–24}

However, to ascertain the relative stabilities of the plausible products of these reactions and estimate the rotational parameters necessary to interpret their rotational spectra, we have carried out new *ab initio* calculations. All stationary points on the reaction pathways explored in this study were fully optimized using the coupled cluster singles and doubles correlated (CCSD) method along with Dunning's augmented correlation consistent polarized valence triple- ζ (aug-cc-pVTZ) basis set.²⁵ The transition states and the minima were mapped using the Quadratic Steepest Descent reaction path.²⁶ All the calculations were carried out using the Molpro 2018.1 *ab initio* program package.²⁷

Fig. 1 illustrates the reaction pathways between CH_2OO and CH_3CHOO with CH_3OH that lead the formation of methoxymethyl hydroperoxide ($\text{HOOCH}_2\text{OCH}_3$, MMHP) and methoxyethyl hydroperoxide ($\text{HOOC}(\text{CH}_3)\text{HOCH}_3$, MEHP), respectively. The first step is the formation of the pre-reactive complex (PRC) which is stabilized by a hydrogen-bonding interaction between CH_3OH hydrogen and the carbonyl oxide terminal oxygen. After complexation, the reactants are positioned for the insertion of the carbonyl oxide into the alcohol O–H bond, which can proceed for two different pathways. Hence, each CI- CH_3OH insertion reaction exhibits two different transition states, distinguished by the orientation of the CH_3OH molecule relative to the CI, giving rise to two different MAHP conformations. Fig. 2 and 3 show the molecular structures for all the stationary points, including pre-reactive complexes, transition states and products, for the CH_3OH reactions with CH_2OO and CH_3CHOO , respectively.

In the case of the *syn*- $\text{CH}_3\text{CHOO} + \text{CH}_3\text{OH}$ another reaction pathway can produce vinyl hydroperoxide ($\text{CH}_2=\text{CHOOH}$), VHP. It consists of an exothermic process where the methanol molecule facilitates the hydrogen transfer from the α -methyl group to the carbonyl oxide terminal oxygen through a double hydrogen shift. This reaction pathway has not been considered in the present work because the formation of VHP is less favorable than the resulting products formed in the insertion

Fig. 1 Energy diagrams for the $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$ (left) and $\text{CH}_3\text{CHOO} + \text{CH}_3\text{OH}$ (right) reactions. All the calculations were performed at the CCSD/aug-cc-pVTZ level of theory. Total energies relative to those of separated molecules are given in parentheses (in kcal mol^{-1}).

Fig. 2 Molecular structures for all the stationary points, including pre-reactive complex, transition states and products, for the $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$ reaction.

Fig. 3 Molecular structures for all the stationary points, including pre-reactive complexes, transition states and products, for the $\text{CH}_3\text{CHOO} + \text{CH}_3\text{OH}$ reaction.

reaction,²⁴ as it occurs in the *syn*- $\text{CH}_3\text{CHOO} + \text{HCOOH}$ reaction.^{28–30}

According to our calculations, the two and four conformers of MMHP and MEHP, respectively, are potentially observable by FTMW spectroscopy since their formation reactions are all exothermic. Accurate molecular rotational constants and electric dipole moment components are necessary to predict the rotational transition frequencies of these species. The values obtained for these parameters at CCSD/aug-cc-pVTZ level of theory are summarized in Tables 1 and 2.

Experimental

The experimental apparatus employed in this investigation has been described in a previous work.³¹ It consists of a Balle-Flygare type Fourier-transform cavity microwave spectrometer³²

Table 1 Rotational constants and electric dipole moment components for the two MMHP conformers calculated at the CCSD/aug-cc-pVTZ level of theory

	MMHP-I	MMHP-II
A/MHz	10 990	13 718
B/MHz	3241	2942
C/MHz	3103	2662
$ \mu_a /\text{D}^a$	2.20	2.91
$ \mu_b /\text{D}$	0.18	0.20
$ \mu_c /\text{D}$	0.26	0.71
$\Delta E/\text{kcal mol}^{-1}$	0 ^b	2.02

^a 1 D $\approx 3.3356 \times 10^{-30}$ C m. ^b Relative energy to that of MMHP-I species.

Table 2 Rotational constants and electric dipole moment components for the four MEHP conformers calculated at the CCSD/aug-cc-pVTZ level of theory

	<i>a</i> -MEHP-I	<i>a</i> -MEHP-II	<i>s</i> -MEHP-I	<i>s</i> -MEHP-II
A/MHz	4688	3963	4757	5753
B/MHz	3120	3565	3065	2604
C/MHz	2230	2057	2264	2155
$ \mu_a /\text{D}^a$	2.38	2.08	2.04	2.72
$ \mu_b /\text{D}$	0.26	0.08	0.48	0.10
$ \mu_c /\text{D}$	0.23	0.51	0.02	0.52
$\Delta E/\text{kcal mol}^{-1}$	0.50 ^b	0.94	0	3.44

^a 1 D $\approx 3.3356 \times 10^{-30}$ C m. ^b Relative energy to that of *s*-MEHP-I species.

operating in the 4–40 GHz frequency region. It is equipped with a pulsed discharge nozzle^{33,34} and a double-resonance setup.³⁵ The frequency measurements have an estimated accuracy better than 3 kHz and the resolution is better than 5 kHz.

In the study of the $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$ reaction the short-lived species were produced in the throat of an electrical discharge of a gas mixture of 1,1-diiodomethane, methanol and oxygen heavily diluted in argon. The gas mixture of 0.3% methanol, 2% O_2 and 97.7% Ar with the total pressure of 1.5 atm was passed through a container filled with liquid 1,1-diiodomethane in order to introduce the precursor molecules with sufficient partial pressures. In the case of CH_3CHOO , 1,1-diiodomethane was replaced by 1,1-diiodoethane, and other experimental conditions were identical. The gas mixture was flowed through a pulsed-solenoid valve that is accommodated in the backside of one of the cavity mirrors and aligned parallel to the optical axis of the resonator. A pulsed voltage of 1.0 kV with 450 μs of duration was applied between electrodes attached at the exit of the nozzle to induce an electric discharge, synchronized with the gas expansion, which triggers the chemical reactions in the precursor mixture. The resulting products generated in the discharge are supersonically expanded and rapidly cooled to a rotational temperature of ~ 2 K and probed by FTMW spectroscopy. Further experiments were carried out with the mono-deuterated species of methanol, CH_3OD , which was prepared by mixing CH_3OH and D_2O .

Results

$\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$

As mentioned before, the target species to be found in the rotational spectrum are the two conformers of MMHP. Prior to the search for these species we checked the production of CH_2OO , and during all the experiments a very strong signal was observed for the $1_{01}-0_{00}$ pure rotational transition of CH_2OO at 23186.49 MHz,³⁶ indicating an efficient production of CH_2OO in the discharged jet.

Referring to the predicted dipole moment components, both MMHP conformers will show strong *a*-type rotational spectrum. Hence, first experiments were devoted to scan the frequency interval between 12 and 15 GHz searching for *a*-type transitions for both conformers. In the initial scans we observed strong

Fig. 4 The FTMW spectra of the $2_{02}-1_{01}$ rotational transitions for the parent species of MMHP-I (left) conformer and *d*-MMHP-I (center) with A and E components indicated, obtained using 100 accumulation shots. (Right) FTMW-MW double resonance spectra of $2_{12}-2_{02}$ rotational transition of MMHP-I conformer showing the A and E internal rotation components. A and E components of the $2_{02}-1_{01}$ at 12579.015 and 12578.950 MHz, respectively, were used to monitor the A and E components of $2_{12}-2_{02}$ rotational transition, respectively.

signals that appeared close to the predicted rotational frequencies for the MMHP-I conformer. These lines, identified as $2_{12}-1_{11}$, $2_{02}-1_{01}$ and $2_{11}-1_{10}$, appeared split into two components, A and E, as a result of the interaction between the molecular overall and internal rotations³⁷ (Fig. 4). MW-MW double-resonance experiments were used for observing additional transitions and thus confirming the assignments of those observed by FTMW spectroscopy (Fig. 4). Very weak *b*- and *c*-type transitions were also observed. Finally a total of 20 pure rotational transitions were measured for this species. All the observed rotational frequencies for A and E components (see ESI[†]) were included in a least-squares fit using the XIAM program³⁸ which is based on the combined axis method with the form given by Woods.³⁹ The analysis rendered the experimental rotational constants together with the internal rotation parameters listed in Table 3. No lines remain unassigned in the scanned regions after the identification of those for the MMHP-I conformer.

The use of deuterated methanol in the further experiments served to confirm the identity of the observed species and the

nature of its formation. By replacing CH_3OH by CH_3OD , we observed rotational transitions for *d*-MMHP-I species ($\text{DOOCH}_2\text{OCH}_3$), where the terminal hydrogen atom in MMHP is substituted by a deuterium atom, which comes from the methanol molecule. The rotational transitions for *d*-MMHP-I species show the A-E splitting like in the parent species. However, no hyperfine effects due to the presence of a deuterium nucleus, with the nuclear quadrupole moment different from zero ($I = 1$), were observed, as seen in Fig. 4. The observed transitions were analyzed using the XIAM program³⁸ and the derived experimental parameters for *d*-MMHP-I species are shown in Table 3.

$\text{CH}_3\text{CHOO} + \text{CH}_3\text{OH}$

As can be seen in Fig. 1, formation of the four MEHP species is exothermic and seems to be as favorable as in the case of the $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$ reaction. During these experiments, strong signals of the $1_{01}-0_{00}$ and $2_{02}-1_{01}$ pure rotational transitions of *syn*- CH_3CHOO and *anti*- CH_3CHOO species were observed at 12362.64 MHz⁴⁰ and 17202.53 MHz⁴¹ respectively, confirming the formation of CH_3CHOO in the discharged jet.

We followed the same strategy used for the MMHP since both species have appreciable μ_a dipole moments. In this manner, we found two series of *a*-type rotational transitions which were finally assigned to the *a*-MEHP-I and *s*-MEHP-I species. For the former a total of 12 *a*-type pure rotational transitions were observed, while 19 transitions, including *a*- and *b*-types, were measured for the latter one. In spite of the fact that both the *a*-MEHP-I and *s*-MEHP-I species have comparable μ_b dipole moment components, the weaker spectrum observed for the *a*-MEHP-I species hampered the observation of *b*-type transitions. Fig. 5 illustrates the $4_{04}-3_{03}$ rotational transitions observed for *a*-MEHP-I and *s*-MEHP-I, which show A-E splitting due to the methyl internal rotation. Analyses of the rotational transitions were carried out using the XIAM program,³⁸ and the derived experimental parameters are depicted in Table 4. No lines remain unassigned in the spectra when all the lines for the *a*-MEHP-I and *s*-MEHP-I conformers were identified. Therefore, no more MEHP species could be observed.

Table 3 Experimental rotational parameters for the observed species of MMHP and its deuterated isotopologue

	MMHP-I	<i>d</i> -MMHP-I
A/MHz	10817.34317(86) ^f	10411.89297(30)
B/MHz	3217.88152(40)	3188.24842(61)
C/MHz	3072.69696(43)	3016.53857(62)
Δ_J/kHz	3.8751(84)	4.106(35)
Δ_{JK}/kHz	-30.519(45)	[-30.519] ^g
δ_J/kHz	0.6532(80)	[0.6532]
V_3/cm^{-1}	541.73(37)	[541.73]
F_0^a/GHz	154.597	154.597
δ^b/rad	0.8771(26)	[0.8771]
ϵ^c/rad	2.030(14)	[2.030]
N^d	40	12
σ^e/kHz	2.4	2.6

^a Rotational constant of the methyl top. Fixed to the *ab initio* value.

^b Angle between the principal axis (*a*-axis) of the molecule and the internal rotation axis. ^c Angle between the principal axis (*a*-axis) of the molecule and the projection of the internal rotation axis onto *bc*-plane.

^d Number of pure rotational transitions included in the fit. ^e Standard deviation of the fit. ^f Values in parentheses denote 1 σ errors, applied to the last digit. ^g Values in brackets refer to values fixed to the those obtained for the parent species.

Fig. 5 The FTMW spectra of the $4_{04}-3_{03}$ rotational transitions for the parent species of *a*-MEHP-I and *s*-MEHP-I conformers showing the A and E components. Both spectra were obtained using 100 accumulation shots.

Table 4 Experimental rotational parameters for the observed conformers of MEHP the isotopic species

	<i>a</i> -MEHP-I	<i>s</i> -MEHP-I	<i>d</i> - <i>s</i> -MEHP-I
<i>A</i> /MHz	4605.7969(36) ^f	4691.0497 (17)	4560.0829(37)
<i>B</i> /MHz	3113.83864 (85)	3055.90066(60)	3029.49989(27)
<i>C</i> /MHz	2212.39680(54)	2248.63486(42)	2222.93333(26)
Δ_J /kHz	1.849(14)	1.705(11)	1.7645(50)
Δ_{JK} /kHz	−4.50(11)	−3.181(59)	[−3.181] ^h
Δ_K /kHz	—	5.90(33)	[5.90]
δ_J /kHz	0.6815(98)	0.5710(52)	[0.5710]
δ_K /kHz	—	0.96(10)	[0.96]
V_3 /cm ^{−1}	650.8(36)	549.00(37)	[549.00]
F_0^a /GHz	153.610	161.825	161.825
δ^b /rad	0.994 ^g	0.6962(36)	[0.6962]
ϵ^c /rad	2.211(35)	2.6191(91)	[2.6191]
N^d	24	38	18
σ^e /kHz	2.7	2.0	1.7

^a Rotational constant of the methyl top. Fixed to the *ab initio* value.

^b Angle between the principal axis (*a*-axis) of the molecule and the internal rotation axis. ^c Angle between the principal axis (*a*-axis) of the molecule and the projection of the internal rotation axis onto *bc*-plane.

^d Number of pure rotational transitions included in the fit. ^e Standard deviation of the fit. ^f Values in parentheses denote 1 σ errors, applied to the last digit. ^g Fixed to the *ab initio* value. ^h Values in brackets refer to values fixed to the those obtained for the parent species.

We carried out experiments using deuterated methanol species to confirm the identity of the observed species. We could measure rotational transitions for the *d*-*s*-MEHP-I species, (DOOC(CH₃)HOCH₃). The experimental parameters determined by the analysis of the spectrum are shown in Table 4. We tried to observe the spectrum for the analogous *d*-*a*-MEHP-I but the trials resulted unfruitful due to the low intensity of the lines.

Discussion

CH₂OO + CH₃OH

The identification of MMHP-I was assisted by the quantum chemical calculations. A good agreement between the experimental and theoretical rotational constants was found, with

maximum relative deviations of about 1.5% for the *A* rotational constant. The assignment of the MMHP-I conformer is reinforced by the observation of the deuterated species *d*-MMHP-I when CH₃OD species is used. This observation also confirms that MMHP is formed *via* the insertion of CH₂OO into the methanol O–H bond (O–D bond when CH₃OD is used). Conformer MMHP-II was not observed in our experiments in spite of the fact that exhaustive spectral searches were carried out. The non-observation of the MMHP-II species can be explained from both kinetic and thermodynamical points of view. The MMHP-I and MMHP-II conformers are formed through independent insertion mechanisms differing only in the TS, which is ~ 0.8 kcal mol^{−1} more stable in the case of the MMHP-I pathway. In addition, the MMHP-I formation is ~ 2 kcal mol^{−1} more exothermic than that for MMHP-II. Although kinetic and thermodynamic data favor the formation of the MMHP-I conformer, the energetic differences of the TSs and the products are tiny compared with the overall exothermicity of the reactions. Our experiments are carried out in a supersonic expansion, and this point must be taken into account since conformational interconversion may occur between the contemplated molecular species. These processes take place in the early stages of the supersonic expansion by collisions between different conformers and the buffer gas molecules. Ruoff *et al.*⁴² have deduced that collisional removal of a higher energy conformer is possible when the isomerization barrier is around 400–500 cm^{−1}, when Ar is used as the carrier gas. In previous works we have reported conformational interconversion between CI species⁴³ through a barrier height of 479 cm^{−1}. As can be seen in Fig. 2, MMHP-I and MMHP-II conformers differ exclusively in the relative orientation of the disposition of the −CH₃ group and then, they present different values of the dihedral angle $\angle$ OCOC. We calculated the potential energy profile for MMHP-II $\rightarrow$ MMHP-I interconversions by scanning the dihedral angle $\angle$ OCOC. An energy barrier of 415 cm^{−1} was found, which is not high enough to preclude the interconversion between these conformers (Fig. 6). Hence, this could be the main reason for the non-observation of conformer MMHP-II in our experiment, which could convert MMHP-II in MMHP-I during the early stages of the supersonic expansion.

The reactivity of CH₂OO toward methanol can be compared to that toward water. Nakajima and Endo^{44,45} investigated the reaction between CH₂OO and water using the same experimental technique as that employed in the present study. They observed coexistence of the PRC, CH₂OO–H₂O, and the reaction product, hydroxymethyl hydroperoxide (HMHP) in the supersonic expansion. The observation of the PRC in the case of the water reaction is easily understood because the TS between the PRC and the reaction product is 9.2 kcal mol^{−1} above the PRC and 2.4 kcal mol^{−1} higher than the separated reactants. In the case of methanol, both TS1 and TS2 are submerged below the reactants and the PRC can easily overcome the TS barriers leading MMHP while little or none of the complexes can survive in the supersonic jet. The observation of MMHP-I species in the reaction of CH₂OO + CH₃OH is obvious in light of the energy results shown in Fig. 1.

Fig. 6 Potential energy profile of MMHP around the $\angle$ OCOC dihedral angle calculated at CCSD/aug-cc-pVTZ level of theory.

On the other hand, for the formation of HMHP from the $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ reaction it has been justified^{4,45–48} by the fact that the water dimer (H_2O)₂ plays a significant role reducing the TS energy. In such reaction, one H_2O molecule of the dimer works just as a catalytic agent.

The analysis of the internal rotation splittings for the MMHP-I conformer allowed us to determine the experimental threefold methyl internal rotation barrier height (V_3) and other structural parameters as collected in Table 3. The experimental values agree well with those predicted *ab initio* which are collected in Table 5. The experimental value for the V_3 barrier, $541.73(37) \text{ cm}^{-1}$ is slightly larger than that predicted theoretically, 509.3 cm^{-1} . Since F_0 value, which is associated with the moment of inertia of the methyl top, could not be determined in the present fit, it was fixed to the value derived from the *ab initio* geometries. The experimental V_3 value found for MMHP-I is very similar to that found by Motiyenko *et al.*⁴⁹ for methoxymethanol molecule ($\text{CH}_3\text{OCH}_2\text{OH}$), which shares the $\text{CH}_3\text{OCH}_2\text{O}$ moiety with MMHP-I ($\text{CH}_3\text{OCH}_2\text{OOH}$). The experimental V_3 value for methoxymethanol found by Motiyenko *et al.* is $545.92(39) \text{ cm}^{-1}$, only 0.8% larger than the value determined for MMHP-I in the present work. In absence of steric hindrances in both species, the V_3 barrier height seems to be governed by similar electronic factors.

Table 5 Theoretical internal rotation parameters for MMHP and MEHP observed conformers

	MMHP-I	<i>a</i> -MEHP-I	<i>s</i> -MEHP-I
V_3^a/cm^{-1}	509.3	592.7	510.0
F_0^b/GHz	154.597	153.610	161.825
δ^c/rad	0.904	0.994	0.718
ϵ^d/rad	1.976	1.957	2.523

^a Internal rotation barrier height calculated at CCSD/aug-cc-pVTZ level of theory. ^b Rotational constant of the methyl top. ^c Angle between the principal axis (*a*-axis) of the molecule and the internal rotation axis. ^d Angle between the principal axis (*a*-axis) of the molecule and the projection of the internal rotation axis onto *bc*-plane.

$\text{CH}_3\text{CHOO} + \text{CH}_3\text{OH}$

As it occurs for MMHP-I, the agreement between the experimental and theoretical values of the rotational constants for MEHP conformers is very good, with maximum relative deviations of about 1.7% for the *A* rotational constant in the case of *a*-MEHP-I. Similarly to the reaction between $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$, the reaction of each *syn*- and *anti*- CH_3CHOO conformers with CH_3OH gives the most stable products, *s*-MEHP-I and *a*-MEHP-I. The formation of *s*-MEHP-I species is preferred due to the fact that *s*-TS1 is lower than *s*-TS2 and *s*-MEHP-I is $\sim 4.4 \text{ kcal mol}^{-1}$ more stable than *s*-MEHP-II. For the *a*-MEHP conformers the energy differences are smaller for the TSs and also between the products. However, the observed *a*-MEHP-I conformer is energetically preferred.

The relative abundances of *s*-MEHP-I and *a*-MEHP-I conformers can be estimated taking into account the observed spectral intensities of the *a*-type rotational transitions (Fig. 5). The intensity of each rotational transition is proportional to the number density of each conformer and the value of the corresponding component of the dipole moment, $N_i \cdot \mu_i$. Considering the predicted values of the dipole moment components (Table 2), the relative abundances have been found to be: *s*-MEHP-I : *a*-MEHP-I = 2.6 : 1, which roughly corresponds to the production ratio of *syn*- and *anti*- CH_3CHOO under our experimental conditions where *syn*- CH_3CHOO is about five times more abundant than *anti*- CH_3CHOO .^{40,41} This abundance ratio for *s*-MEHP-I/*a*-MEHP-I contrasts with the reaction paths from Fig. 1, where the *s*-PRC/*s*-TS1 energy gap is 2 times larger than that for *a*-PRC/*a*-TS1 with *a*-TS1 submerged below the reactants while *s*-TS1 is slightly above the reactants. The inconsistency between the theory and our experimental results can be explained considering the termolecular reaction of *syn*- $\text{CH}_3\text{CHOO} + 2\text{CH}_3\text{OH}$. Chao *et al.*²² reported both experimentally and theoretically an enhancement on the reactivity of *syn*- CH_3CHOO toward CH_3OH when a second methanol molecule is involved in the reaction. The assistance of these molecules as catalysts is reflected in a large decrease in the energy gap PRC/TS, which increases the reactivity of *syn*- CH_3CHOO toward CH_3OH . As shown by Chao *et al.*²² the formation of *s*-MEHP-I proceeds *via* a 7-membered-ring transition state structure and the reaction involves transfer of the H atoms and formation of a CO bond. Hence, our experimental results can be understood after considering the termolecular reaction of *syn*- $\text{CH}_3\text{CHOO} + 2\text{CH}_3\text{OH}$, which predominate over bimolecular reactions under certain conditions like in other CI reactions toward hydrogen-bonding molecules. Similar catalytic effects have been reported to occur when a second water molecule participates in the $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ ^{46–48} and *anti*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$ ⁵⁰ reactions.

The present results can be compared to those reported by Cabezas and Endo⁵¹ for the FTMW study of the $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$ reaction. In that case, the *syn*- CH_3CHOO - H_2O PRC was observed together with two conformers of hydroxyethyl hydroperoxide (HEHP) formed from the reaction of *anti*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$. These results agreed with the theoretical calculations since the TS barrier for the *syn*- $\text{CH}_3\text{CHOO} + \text{H}_2\text{O}$ pathway was

higher than that for *anti*-CH₃CHOO + H₂O. These energy calculations for the CH₃CHOO + H₂O reaction are almost identical to those reported in this work for the CH₃CHOO + CH₃OH reaction. However, the experimental results from the two studies are very different with no MEHP formed from *syn*-CH₃CHOO while *s*-MEHP-I is more abundant than *a*-MEHP-I. This could be explained, as mentioned before, considering a mediation of a third molecule in the reaction of *syn*-CH₃CHOO + CH₃OH which does not occur in the *syn*-CH₃CHOO + H₂O reaction.

The rotational transitions for both *a*-MEHP-I and *s*-MEHP-I conformers display *A-E* splitting due to the internal rotation of only one methyl, despite the fact that two methyl groups exist in the MEHP molecule. Table 5 shows the theoretical values calculated for the V_3 barrier heights for the O-CH₃ methyl tops of *a*-MEHP-I and *s*-MEHP-I conformers. Those for the other -CH₃ top, attached to the carbon atom, were calculated to be 938.0 and 783.9 cm⁻¹ for *a*-MEHP-I and *s*-MEHP-I conformers, respectively. These values are too high to induce the appearance of internal rotation splittings. However, in the spectral analyses we considered both alternatives, O-CH₃ and C-CH₃, and only when we assigned the *A-E* splitting to the O-CH₃ tops the results were reasonable. The analysis enabled us to determine the V_3 barrier heights together with some structural parameters such as δ and ε (see Table 4). The agreement between the theoretical and experimental values is fairly good and confirms the assignment of the internal rotation splittings. The experimental V_3 barrier heights found for the *a*-MEHP-I and *s*-MEHP-I conformers are 650.8(36) and 549.00(37) cm⁻¹. The barrier height for *s*-MEHP-I is very similar to that determined for the MMHP-I conformer, 541.73(37) cm⁻¹, which indicates that the surroundings for the methyl tops in both species are almost identical. In contrast, for *a*-MEHP-I the V_3 value is $\sim 20\%$ larger than those for the *s*-MEHP-I and MMHP-I species. The steric hindrance caused by the orientation of the C-CH₃ methyl top in the *a*-MEHP-I species seems to be the main factor that enhances the internal rotation barrier height for this conformer.

Conclusions

In the present study, we reported the first direct spectroscopic detection of α -methoxyalkyl hydroperoxides (MAHPs) as the nascent products from the atmospheric reactions between the CH₂OO and CH₃CHOO Criegee intermediates and methanol. Using FTMW spectroscopy supported by high level *ab initio* calculations, one and two conformers of methoxymethyl hydroperoxide (MMHP) and methoxyethyl hydroperoxide (MEHP), respectively, were identified in the gas phase. MMHP-I conformer is formed in the insertion reaction of CH₂OO into the methanol O-H bond, which is confirmed by isotopic substitution experiments. The non observation of further MMHP conformers is justified by kinetic and thermodynamic data and by the existence of conformational relaxation processes. Both *anti* and *syn* conformers of CH₃CHOO react with methanol

and produce the *a*-MEHP-I and *s*-MEHP-I conformers, respectively, being *s*-MEHP-I ~ 2.6 times more abundant than *a*-MEHP-I. These observed abundances cannot be explained by theory when only the bimolecular reaction paths of *syn*-CH₃CHOO + CH₃OH are considered. However, when the termolecular reaction of *syn*-CH₃CHOO + 2CH₃OH is contemplated, the experimental observations may be understood. Although it is not clear whether methanol monomer or dimer can be attributed to the production of MEHP, rotational spectroscopy showed a critical evidence that MEHP is produced in similar ratios when *syn*- and *anti*-CH₃CHOO react with methanol vapor.

Conflicts of interest

There are no conflicts to declare.

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