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**Title:**

Criegee Intermediate–Alcohol Reactions, A Potential Source of Functionalized Hydroperoxides in the Atmosphere

**Author list:**

Max R. McGillen[a,1], Basile F.E. Curchod[a], Rabi Chhantyal-Pun[a], Joseph M. Beames[b], Nathan Watson[b], M. Anwar H. Khan[a], Laura McMahon[a], Dudley E. Shallcross[a] and Andrew J. Orr-Ewing[a,1]

[a]School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK; [b]School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

[1]To whom correspondence may be addressed. Email: max.mcgillen@gmail.com, a.orr-ewing@bristol.ac.uk

**Keywords:**

Criegee, alcohol, kinetics, atmospheric chemistry, non-Arrhenius, hydroperoxide

## Abstract

Ozonolysis, the mechanism by which alkenes are oxidized by ozone in the atmosphere, produces a diverse family of oxidants known as Criegee intermediates (CIs). Using a combination of newly acquired laboratory data and global atmospheric chemistry and transport modelling, we find that the reaction of CIs with alcohols – a reaction that was originally employed to trap these reactive species and provide evidence for the ozonolysis mechanism nearly 70 years ago – is occurring in Earth's atmosphere and may represent a sizeable source of functionalized hydroperoxides therein. Rate coefficients are reported for the reactions of $CH_2OO$ and $(CH_3)_2COO$ + methanol and that of $CH_2OO$ + ethanol. Substitution about the Criegee intermediate is found to have a strong influence over the reaction rate, whereas substitution on the alcohol moiety does not. Although these reactions are not especially rapid, both the precursors to CIs and alcohols have large emissions from the terrestrial biosphere, leading to a high degree of collocation for this chemistry. We estimate that the products of these reactions, the *α*-alkoxyalkyl hydroperoxides (AAAHs) have a production rate of ~30 Gg $yr^{-1}$. In order to assess the atmospheric lifetime of AAAHs, we used the nuclear ensemble method to construct a UV absorption spectrum from the four lowest energy conformers identified for a representative AAAH, methoxymethyl hydroperoxide. The computed absorption cross section indicates that these compounds will be lost by solar photolysis, although not so rapidly as to exclude competition from other sinks such as oxidation, thermal decay and aerosol uptake.


## 1. Introduction

Criegee intermediates (CIs), also known as carbonyl oxides, are a family of oxidants produced in Earth's atmosphere through alkene ozonolysis. The identity of a CI is determined by the alkene reagent, and as a consequence of its zwitterionic character, may exist in several forms with significant barriers to rotation between conformers.[1] In the ozonolysis of isoprene, for example, nine possible Criegee intermediates are produced.[2] The corollary of this is that the variety of CIs encountered in the atmosphere may exceed that of alkenes. Ozonolysis forms CIs that possess a range of internal energies, a varying proportion of which possess sufficient excitation for prompt decomposition. The remainder may be either collisionally stabilized or formed in a stabilized state. These stabilized CIs will be sufficiently long-lived with respect to unimolecular processes that they may also engage in bimolecular reactions.

Laboratory studies have identified a large diversity in the bimolecular reactivity among CIs. In the case of water dimer, $(H_2O)_2$, a rapid reaction ($k_{298} = 7.4 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) is observed with formaldehyde oxide, $CH_2OO$,[3] yet no significant reactivity ($k_{298} = <1.5 \times 10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) is observed for acetone oxide, $(CH_3)_2COO$.[4] Conversely, both CIs react rapidly with $SO_2$, with $(CH_3)_2COO$ exhibiting a faster reaction rate.[4-5] It is therefore apparent that the reactivity of a given CI depends strongly upon both its structure and the identity of its reaction partner.

Despite having a low tropospheric concentration, estimated to be $5 \times 10^{4\pm1}$ molecule $cm^{-3}$,[6] CIs have been identified as important oxidants of both $SO_2$[7-8] and organic acids.[9-10] Furthermore, among atmospheric oxidants, CIs are unusual in their capacity to add both carbon and oxygen mass to the co-reactant through 1,3-dipolar cycloaddition[11-12] and insertion mechanisms,[13-14] and therefore have the potential to produce low volatility products in comparatively few reaction steps, which may facilitate secondary organic aerosol (SOA) formation.

Alcohols are a prevalent class of volatile organic compounds in the atmosphere and have terrestrial biogenic sources,[15-16] of which tropical rainforests are among the largest. Since the highest flux of CIs is predicted to occur in the equatorial regions,[9, 17] collocation is expected between CIs and alcohols in the troposphere, and the reactions between these species therefore warrant investigation. Such reactions are well known to synthetic chemists and have found utility in the preparation of $\alpha$-alkoxyalkyl hydroperoxides (AAAHs).[18] Similarly in the gas phase, AAAHs have been identified in the reaction of CIs ($CH_2OO$, *syn*-/*anti*-tridecanal oxide) with alcohols (methanol, 2-propanol), all of which were studied using a static reaction chamber.[19-20] Tobias and Ziemann[20] reported a relative rate coefficient for these reactions, where heptanoic acid was used as a reference compound. However, few direct kinetic data are available and in order to address this knowledge gap, a systematic study of the following reactions is conducted:

$CH_2OO + CH_3OH \rightarrow$ products (1)

$CH_2OO + C_2H_5OH \rightarrow$ products (2)

$(CH_3)_2COO + CH_3OH \rightarrow$ products (3)

Reaction 1 is an insertion reaction and the product has been identified as methoxymethyl hydroperoxide (MMHP).[19] A calculated UV absorption spectrum of MMHP is presented, which allows its atmospheric photolysis lifetime to be assessed. This spectrum is found to closely resemble the experimentally measured spectra of analogous hydroperoxide species, and given the apparently generic similarity between these hydroperoxides, MMHP is used to represent the panoply of AAAHs that are expected to form from the reactions of larger, naturally occurring CIs with methanol. The atmospheric implications of these reactions are investigated through global chemistry transport modelling.

## 2. Methods

**2.1. Experimental measurements.** Rate coefficients for Reactions 1–3 were determined at temperatures from 254–329 K and total pressures from 10–100 Torr using cavity ring-down spectroscopy (CRDS) to obtain temporal decay profiles of a flowing mixture of $CH_2OO$ or $(CH_3)_2COO$ in the presence of a known excess of either methanol or ethanol. All rate coefficients

were measured under *pseudo*-first-order conditions, where [alcohol] >> [CI]. The temperature of the reactor was controlled by circulating a heated or cooled fluid through an outer jacket, with a second insulating jacket employed to reduce temperature gradients across the reaction volume. A brief description of the apparatus and experimental technique is given below, with a fuller account provided by Chhantyal-Pun et al.[5, 10]

Criegee intermediates, $CH_2OO$ and $(CH_3)_2COO$ were generated through the photolysis ($\lambda$ = 355 nm) of alkyl *gem*-diiodide precursors in the presence of excess $O_2$ according to the methodology of Welz et al.:[21]

$$CR_2I_2 + h\nu \rightarrow CR_2I + I \quad (4)$$

$$CR_2I + O_2 \rightarrow CR_2OO + I \quad (5)$$

where R = H or $CH_3$.

Signals of $CH_2OO$ or $(CH_3)_2COO$ were probed using CRDS, the optical cavity of which was positioned at an angle of 3.8° with respect to the photolysis beam, providing a 7.6 cm long interaction region. The probe beam wavelength of 355 nm overlapped the broad and intense $\widetilde{B}\ ^1A' \leftarrow \widetilde{X}\ ^1A'$ electronic absorption bands of these CIs. Temporal decay profiles of CIs were generated by varying the delay time (i.e. reaction time) between the photolysis and probe beams. Under our experimental conditions, typical ring-down times (<6 μs) were much shorter than the timescales over which kinetic measurements were performed (1–14 ms).

These profiles were fitted with a simultaneous first- and second-order decay fit function shown in Eq. I:[5]

$$\Delta\kappa(t) = \frac{k_p}{\frac{k_p}{\Delta\kappa(t_0)}e^{k_p t} - k'\left(\frac{2L}{cd}\right) + k'\left(\frac{2L}{cd}\right)e^{k_p t}} \quad (I)$$

where $\Delta\kappa(t)$ is the change in ring-down decay rate constant at delay time $t$ caused by the photolysis laser, $L$ is the cavity length (100 cm), $d$ is the photolysis-probe laser overlap length (7.6 cm), $c$ is the speed of light, $k_p$ is the *pseudo*-first-order rate coefficient with respect to the alcohol reagent, $k' = k_{obs}/\sigma_{355\ nm}$ is the second-order decay rate coefficient for the self-reaction of the CI scaled by its absorption cross section at 355 nm. Because $k'$ is temperature dependent, a series of decay profiles were measured in the absence of alcohol over a range of temperatures, and these data were used to define a temperature-dependent function of the self-reaction, $k'(T)$, for use in this equation.

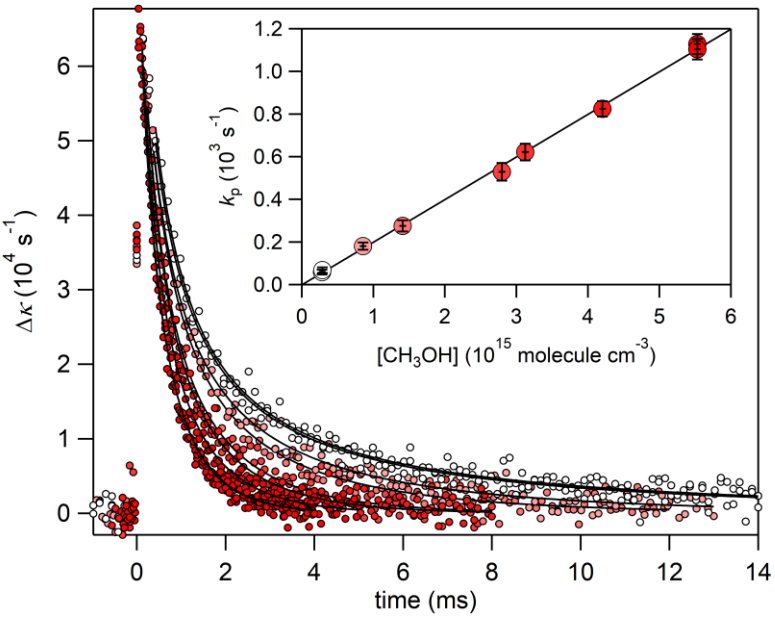



**Fig. 1.** A series of kinetic decay traces acquired at 254 K showing progressively faster decays of $CH_2OO$ as methanol concentration is increased. Solid lines are fits according to Eq. I, from which the *pseudo*-first-order rate coefficients, $k_p$, are obtained. These values are plotted as a function of $[CH_3OH]$ in the inset, the slope of which yields the bimolecular rate coefficient. Error bars in the inset represent the 2σ statistical uncertainty of the fits.

Alcohols were introduced into the reaction volume from a dilute bulb using a calibrated flow controller (MKS) over a range of concentrations, typically spanning a factor of ≥20. Concentrations were determined from the ideal gas law using the known mass flow rates from manometrically prepared bulbs, reactor temperature and pressure. Bimolecular rate coefficients for Reactions 1–3 were obtained from the slope of an error-weighted linear least-squares fit of $k_p$ vs [alcohol]. In experiments with $CH_3OD$ and $CD_3OD$, since they possess the labile O–D moiety, $D_2O$ was bubbled through the gas lines, mass flow controller and reactor for 24 hours prior to data acquisition.

**2.2. Materials.** Methanol (≥99.9%), ethanol (≥99.5%) $CD_3OD$ (≥99.8 atom % D), $CD_3OH$ (99.8 atom % D), $CH_3OD$ (99.5 atom % D), diiodomethane (99%) (Sigma-Aldrich), 2,2-diiodopropane (a high-purity sample was synthesized at the University of Edinburgh, see SI for proton and carbon NMR spectra) were subjected to several freeze-pump-thaw cycles prior to their introduction into darkened 10 L Pyrex bulbs. $D_2O$ (99.9 atom % D) (Sigma-Aldrich) was degassed but otherwise used as supplied. High purity compressed gases $N_2$ (diluent and bath gas) and $O_2$ (reagent in Reaction 5) (Air Liquide) were used as supplied.

**2.3. Computational calculations.** For energy calculations, stationary points on the reaction pathways were optimized using DFT//B3LYP/aug-cc-pVTZ, all of which were verified through vibrational frequency calculations, and all transition states were linked to their respective minima through

intrinsic reaction coordinate calculations. All geometries were generated using the Gaussian09 package.[22] Single point energy calculations were performed at each stationary point using DF-HF//DF-LCCSD(T)-F12a/aug-cc-pVTZ. Both density fitting integral approximations, and local correlation methods offer significant advantages in reducing computational cost when scaling to larger molecular systems, and were used here to provide high accuracy molecular energies. These calculations also include explicit electron correlation through use of the F12 ansatz, where F12a was chosen as the most appropriate treatment for this basis set. All energy calculations were performed using MOLPRO.[23] Recent calculations suggest that the CI moiety transitions from predominantly zwitterionic to biradical character during the course of a bimolecular reaction,[24] which represents a major challenge for most computational electronic structure techniques. Multireference computational methods could be used in future for more detailed reaction pathway characterisation.

For calculation of absorption cross sections, geometry optimizations of MMHP were conducted at the MP2 level of theory[25-28] using an aug-cc-pVTZ basis set[29] with Gaussian09[22] for four conformers (see SI for details about the conformers and the level of theory employed). Frequency calculations confirmed that all localized extrema are actual minima of the ground state potential energy surface. A photoabsorption cross section was then constructed for each conformer using the semiclassical[30-32] nuclear ensemble method as implemented in Newton-X version 1.4.[33-34] The nuclear ensemble technique samples a set of $N_n$ nuclear geometries (200 in this case) from an approximate quantum distribution in the ground-electronic state. Excitation energies ($\Delta E_{0n}$) and oscillator strengths ($f_{0n}$) are then computed for each sampled geometry $\boldsymbol{R}_l$ and a photoabsorption cross section $\sigma(E)$ is constructed by summing all the contributions using the equation:

$$\sigma(E) = \frac{\pi e^2 \hbar \gamma}{2mc\varepsilon_0} \sum_n^{N_s} \frac{1}{N_n} \sum_l^{N_n} f_{0n}(\boldsymbol{R}_l)\, g(E - E_{0n}(\boldsymbol{R}_l), \delta) \quad \text{(II)}$$

$N_s$ is the total number of excited electronic states considered (1 in the present case) and $g(E - E_{0n}(\boldsymbol{R}_l), \delta)$ corresponds to a Lorentzian function with a width $\delta = 0.05\ eV$. The nuclear ensemble technique provides band shapes and heights, but it is important to note that it does not reproduce vibronic progressions.

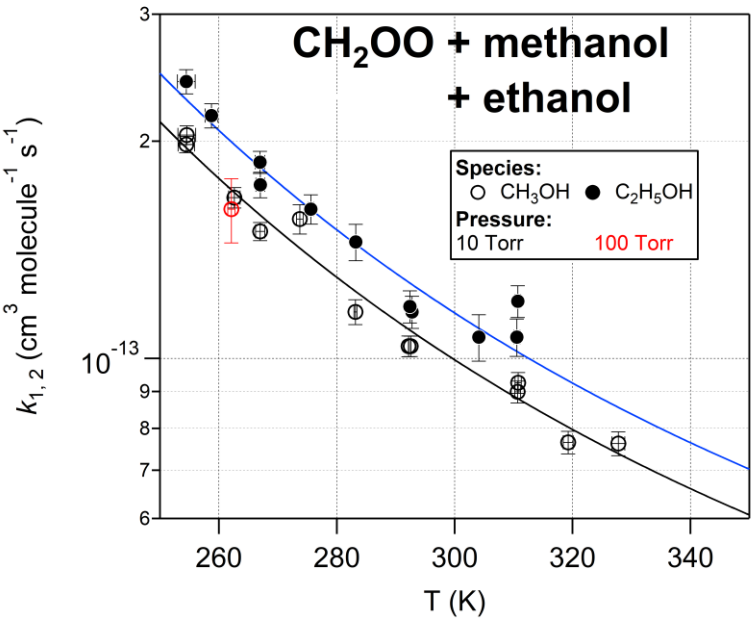
The excitation energies and oscillator strengths for the transition to the first electronic state ($S_1$) were computed for all sampled geometries with the spin-component scaling second-order approximate coupled cluster (SCS-CC2) method,[35-37] using an aug-cc-pVDZ basis set, with the program Turbomole v6.4.[38] This level of theory was benchmarked against equation-of-motion coupled cluster singles and doubles (EOM-CCSD),[39] and a detailed comparison is presented in the supporting information.

**2.4. Atmospheric chemistry and transport modelling.** The atmospheric sources of AAAHs were quantified by incorporating the kinetic measurements of this study into the STOCHEM-CRI global

atmospheric chemistry and transport model.[40] In the model, CIs are generated from 6 representative alkenes (ethene, propene, (*Z*)-2-butene, isoprene, $\alpha$-pinene and $\beta$-pinene). Since many more alkenes are emitted to the atmosphere than are present in the model, this limited selection is weighted to reflect the alkene functionality of the total biogenic alkene flux into the atmosphere,[41] which allows for a realistic distribution of CIs at a reduced computational cost. Both the model and the methodology for generating CI fields have been used previously.[9, 42] However, based on the availability of new experimental measurements and quantum calculations, these CI fields have been updated.[10] A full account of the stabilized CI yield from ozonolysis, the branching ratio between CIs, the unimolecular loss rate and rate coefficients for reactions with $H_2O$, $(H_2O)_2$ and methanol for each of the CIs contained within the model is provided in Table S4. By considering the production through the reactions of CIs with alcohols and the losses by photolysis and reaction with OH (by analogy to other hydroperoxides), the concentration of AAAH can be estimated in the model.

## 3. Experimental results

Experiments were conducted to measure the rates of reaction of CIs with methanol and ethanol. All kinetic data were fitted using a combined 1$^{st}$- and 2$^{nd}$-order expression, Eq. I (see Section 2.1) and temporal profiles of CIs were well described by these fits in all cases (Fig. 1 shows a representative dataset). In the experiments in which $(CH_3)_2COO$ was a reagent, a more rapid unimolecular decay occurred (~300 $s^{-1}$)[43], which manifested itself as an intercept in plots of $k_p$ vs [methanol]. Rate coefficients were observed to be pressure independent from 10–100 Torr ($N_2$). Rate coefficient data are plotted as a function of temperature in Figs. 2–3, and show that Reactions 1–3 each exhibit a negative temperature dependence, together with curvature, which is quite pronounced in the case of Reaction 3. Kinetic data obtained in this study are presented in Tables S1–3, together with the experimental conditions that were employed; errors in rate coefficients are expressed as 2$\sigma$ statistical uncertainty, other errors are provided at 1$\sigma$.




209

210 **Fig. 2.** The bimolecular rate coefficients for the reactions of methanol and ethanol with $CH_2OO$
211 exhibit a similar negative temperature dependence. Solid lines represent modified Arrhenius fits to
212 data (see Eqs. III and IV). Error bars represent $2\sigma$ statistical uncertainty for rate coefficients and $1\sigma$ for
213 temperature.

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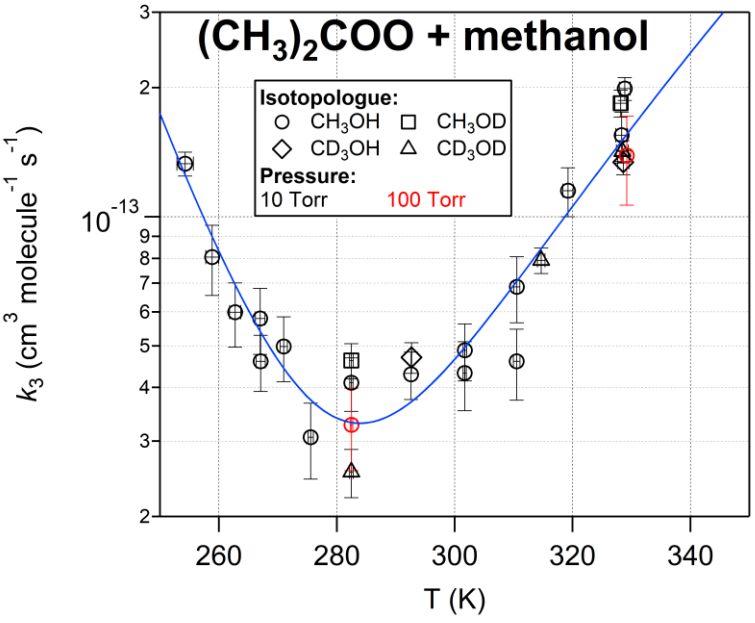



215

216 **Fig. 3.** The bimolecular rate coefficient for the reaction of methanol with $(CH_3)_2COO$ exhibits both
217 positive and negative temperature dependent regimes. The solid line represents a sum of two $AT^n$-type
218 expressions (see Eq. V). Error bars represent $2\sigma$ statistical uncertainty for rate coefficients and $1\sigma$ for
219 temperature.

220

221

### 3.1. Reactions of $CH_2OO$ + $CH_3OH$ and $C_2H_5OH$

Reaction 1, $CH_2OO$ + $CH_3OH$, is the simplest of the reactions studied, with both reactants possessing one carbon atom. This reaction is expected to proceed through an insertion mechanism which produces $CH_3OCH_2OOH$ (MMHP).[19]

Fig. 2 shows the bimolecular rate coefficient, $k_1$, plotted as a function of temperature. These data are tabulated together with the experimental conditions in Table S1. From Fig. 2, it is apparent that there is a negative temperature dependence, no apparent dependence on pressure and that individual determinations of $k_1$ are highly reproducible. The high precision of the data allows a weak curvature to be observed, which was fitted using a modified Arrhenius expression, yielding the following expression for the temperature dependence of $k_1$:

$k_1(T) = 3.7\pm1.4 \times 10^{-21}\ T^2 \exp(1710\pm103/T)$ (III)

The overall negative temperature dependence suggests that Reaction 1 proceeds through a pre-reactive complex in the entrance channel.[44]

Reaction 2, $CH_2OO$ + $C_2H_5OH$, was found to possess a similar rate coefficient to Reaction 1. Fig. 2 also shows $k_2$ vs temperature, with kinetic data and experimental conditions tabulated in Table S2. The precisions of the rate coefficient measurements approach those of Reaction 1, allowing observation of some curvature in the temperature dependence, which was fitted with the following modified Arrhenius expression:

$k_2(T) = 4.2\pm2.2 \times 10^{-21}\ T^2 \exp(1717\pm145/T)$ (IV)

Both the *A*-factor and the activation energy ($E_a/R$) are similar to those obtained for Reaction 1, indicating that the carbon chain length on the alcohol does not have a strong influence over the reaction rate. Again, the formation of a pre-reactive complex in the initial reaction step is expected to be responsible for the negative temperature dependence observed.

### 3.2. Reaction of $(CH_3)_2COO$ + $CH_3OH$

Fig. 3 shows a plot of $k_3$ vs temperature for Reaction (3) $(CH_3)_2COO$ + $CH_3OH$, with kinetic data and experimental conditions provided in Table S3. In contrast to Reactions 1 and 2, Reaction 3 shows an overall slower reaction rate with a strongly curved temperature dependence. In this instance, the curvature is such that the data are best described with a more complicated function, and a sum of two expressions was used to describe both the positive and negative temperature-dependent components to the overall rate coefficient:

$$k_3(T) = 6.07 \times 10^{-33} T^{3.87} \exp(5852/T) + 5.82 \times 10^{-16} T^{2.92} \exp(-3741/T) \text{ (V)}$$

Because of the complexity of the above expression, these optimized values should not be considered to form a unique solution, and *A*-factors and activation energies should be treated with caution. However, taken at face value, the temperature dependencies therein are both highly positive and negative respectively. One interpretation of the positive temperature dependent component of this reaction is the agency of a hydrogen abstraction mechanism that operates parallel to the generally accepted insertion mechanism that forms AAAHs in these reactions.[18-20, 45] To investigate this possibility further, rate coefficients were determined for a suite of deuterated isotopologues of methanol. As can be seen from Fig. 3, no significant differences were observed between the isotopologues. This result indicates that hydrogen abstraction does not make a significant contribution to the overall rate coefficient under these conditions, and implies that the differences are likely to result solely from dissimilarities on the potential energy surfaces for the insertion reactions (see the following section for further discussion). In a pre-reactive complex-forming reaction such as this, there remains the potential for interfering absorption by the complex at the probe wavelength to affect the retrieved decay profiles. A kinetic analysis is presented in the SI, from which we conclude that such an outcome is unlikely.

## 4. Discussion and supporting calculations

The similarity between $k(T)$ for Reactions 1 and 2 indicates that the size of the alkyl chain of the alcohol has little effect on the rate coefficient for these reactions, and any differences appear to be limited to the *A*-factor. That deuteration of the alcohol moiety has no discernible effect on Reaction 3 further implies that H/D transfer does not have a strong impact on the overall rate coefficient. In contrast, the substitution about the CI has a large influence over the reaction rate. One way of rationalizing this observation is that the barrier to forming the transition state that leads to products is higher in the case of Reaction 3. This hypothesis is supported by potential energy calculations for Reactions 1 and 3, shown in Fig. 4, which suggest that both Reactions 1 and 3 form pre-reactive complexes that are stabilized by a single hydrogen bond between the hydrogen of the alcohol moiety and the terminal oxygen of the CI moiety. The barrier to forming AAAH products is found to be submerged in both Reactions 1 and 3, however, in the latter case, the transition state is very close to the energy of reactants. Furthermore, the pre-reactive complex is ~6 kJ mol$^{-1}$ lower in energy than in Reaction 1, demonstrating that the local minimum in which the pre-reactive complex resides is significantly deeper in the case of Reaction 3.

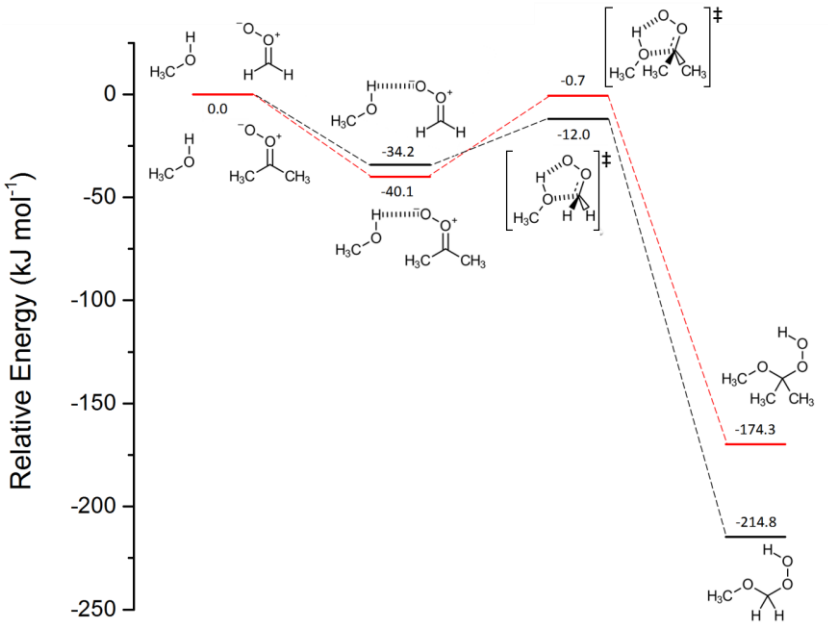



**Fig. 4.** Potential energy calculations for the reactions of methanol with $CH_2OO$ (black) and $(CH_3)_2COO$ (red). For $CH_2OO$, a lower barrier is observed, whereas for $(CH_3)_2COO$, the barrier that is encountered by reactants coming out of the pre-reactive complex energy well is significantly higher, which might explain the complicated temperature dependence observed for this reaction. Optimized structures for each of these species and complexes can be found in the SI.

No absolute kinetic measurements are available in the literature with which Reactions 1–3 can be compared, although the rate of reaction between methanol and the $C_{13}$ CIs produced from 1-tetradecene ozonolysis has been determined relative to the reaction with heptanoic acid [20]. It is necessary to make several assumptions to put this relative rate onto the absolute scale (see Section 6 for a full treatment), and once performed, yields rate coefficients that are a factor of ~2 larger than the absolute determinations of this work. Given that at least some of this difference may be physical between the $C_{13}$ CIs and the smaller CIs of this work, and that no major cancellation of errors results from these assumptions, the level of agreement is satisfactory. This finding indicates that larger CIs – more representative of those formed in the atmosphere by ozonolysis and less likely to be consumed rapidly by water – behave in a similar way to the smaller CIs that are presented here. This comparison also shows that static chamber-based measurements can provide a suitable alternative to these absolute measurements, which become rapidly limited by vapour pressure as the size of carbon backbone of alkyl *gem*-diiodides increases[46].

## 5. Atmospheric implications.

Based on the large flux of methanol to the atmosphere, it is clear that Reactions 1 and 3 cannot represent an important tropospheric methanol sink. Accordingly, this discussion focusses on the products of these reactions, the AAAHs. Two main loss processes are considered here, the photolytic loss and the loss by reaction with OH radicals.

The UV absorption spectra of these peroxides have not been studied previously and in order to assess their photolysis lifetimes, a calculated spectrum for MMHP was obtained through the nuclear ensemble method described in the Methods section. Fig. 5 compares this calculated spectrum with experimentally determined spectra for similar hydroperoxides available in the literature [47-48]. MMHP was found to possess 4 low energy conformers, and the spectrum in Fig. 5 represents an average that is weighted according to the abundance of each of these conformers (for the conformer-specific spectra and their free energies, see SI). A striking similarity was observed between the computed absorption spectrum of MMHP and the most closely analogous compound, hydroxymethyl hydroperoxide, and as with this compound, the photolysis lifetime is therefore expected to be ~4 days [48].

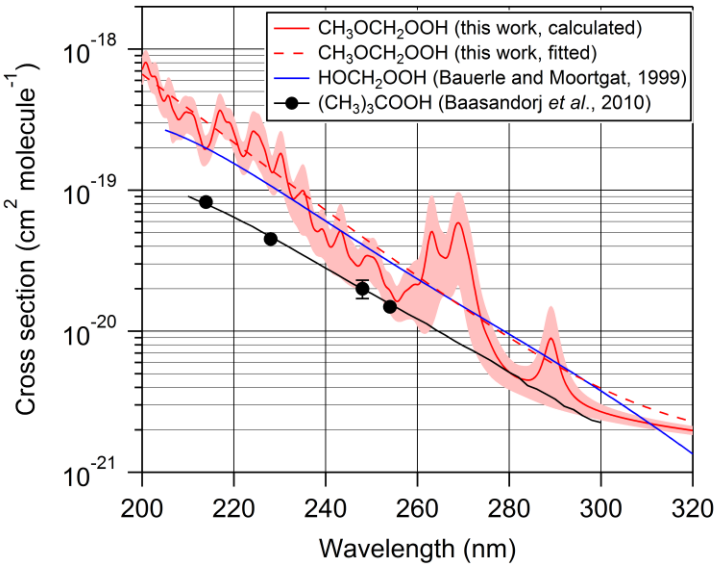



**Fig. 5.** Calculated UV absorption cross section for the simplest $\alpha$-alkoxyalkyl hydroperoxide (AAAH), methoxymethyl hydroperoxide (MMHP). A close similarity is observed between MMHP and the literature measurement for hydroxymethyl hydroperoxide, suggesting a commonality in the photochemistry of AAAHs.

This lifetime is long enough for oxidation by OH to become competitive. Although no rate coefficients of AAAHs + OH are available in the literature, measurements of other hydroperoxides indicate that the peroxidic hydrogen will be the dominant reactive site, with overall rate coefficients that range from ~2–6 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at room temperature[47, 49-52] and no clear dependence on alkyl substitution. With the additional ether functionality of AAAHs, it is expected that these hydroperoxides will tend towards the more reactive end, and if 6 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ is representative of the AAAHs, this leads to a lifetime of ~2 days assuming an average OH concentration of 1 × $10^6$ molecule $cm^{-3}$. Reaction with OH will therefore be the main removal process, but photolysis will also be significant.

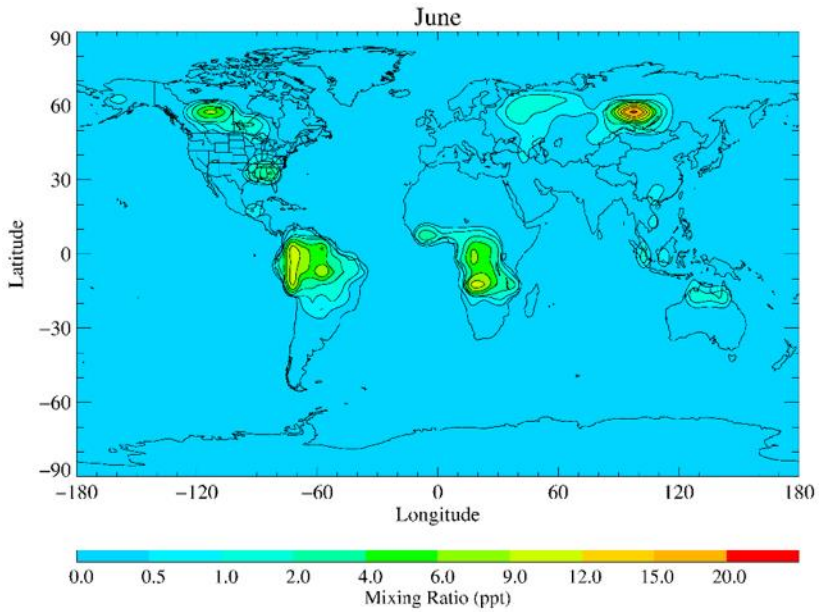



**Fig. 6.** The global distribution of AAAHs formed in the atmosphere for the month of June. A strong colocation between AAAHs and the productive forested regions is observed, which is a consequence of the large terrestrial biospheric source of methanol and alkenes in these areas.

These atmospheric sinks of AAAHs were incorporated into a global chemistry transport modelling simulation, together with the source terms described in the Section 2.4 (details on the rate coefficients employed can be found in Table S4). Global mixing ratios of AAAHs are provided in Fig. 6 for the month of June, when the biogenic emissions of methanol and CI precursors from the boreal forests are at a maximum. Fig. 7 shows monthly production rates, indicating that the tropical forests represent a dominant source throughout the year (24 Gg $yr^{-1}$), with a minimum between July and September, during the dry season in the southern tropics. By contrast the boreal forests produce a maximum between June and August, falling off rapidly on either side, with an annual flux of 3 Gg $yr^{-1}$. Temperate forests are the smallest source of AAAHs considered, with a production rate of 2 Gg $yr^{-1}$, showing a similar seasonality to the boreal forests.

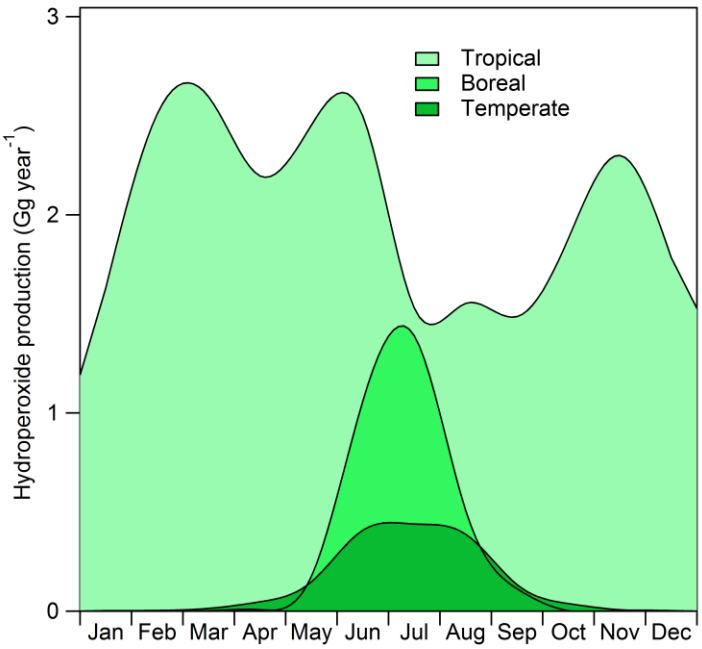



**Fig. 7.** The production of AAAHs over the course of a year. Whereas tropical forests represent a dominant source throughout the year, boreal and temperate forests only contribute significantly during the northern hemispheric summer.

Although the present calculations suggest that AAAHs will constitute a radical source in the troposphere, the formation of larger, more functionalized AAAHs derived from the reactions of more complicated CIs, alcohols, or the secondary oxidation of primary AAAHs may have a subtler role to play in the formation of SOA.

**6. Comparison with literature measurements.** Tobias and Ziemann[20] reported a room temperature relative rate for the reaction of a $C_{13}$ Criegee intermediate produced from 1-tetradecene ozonolysis:

$$1\text{-}C_{14}H_{28} + O_3 \rightarrow \textit{syn}\text{-}/\textit{anti}\text{-}C_{13}H_{26}OO + CH_2O \quad (6a)$$

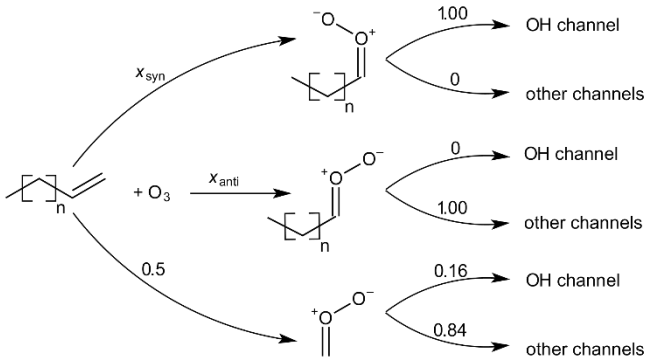
$$\rightarrow CH_2OO + C_{13}H_{26}O \quad (6b)$$

where heptanoic acid was employed as a reference reagent. Given that Reaction 6 produces both *syn* and *anti* conformers, this relative rate is interpreted as follows:

$$\frac{\left(k_{syn\text{-}C_{13}H_{26}OO + CH_3OH} \cdot x_{syn}\right) + \left(k_{anti\text{-}C_{13}H_{26}OO + CH_3OH} \cdot (1 - x_{syn})\right)}{k_{syn\text{-}/anti\text{-}C_{13}H_{26}OO + \text{heptanoic acid}}} = 0.0013 \text{ (VI)}$$

Comparison of the current results with their measurement, necessitates several assumptions. Firstly, $k_{syn\text{-}/anti\text{-}C_{13}H_{26}OO + \text{heptanoic acid}}$ is taken to be a generic rate coefficient of $1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for all organic acid + CI reactions, with no conformer dependence ascribed [9]. Secondly, in the absence

of experimental data, an assumption must be made regarding the molar branching ratio for formation of the *syn* and *anti* CIs, $x_{syn}$ and $1-x_{syn}$ in Eq. VI. One way to approach this is to take the OH yield from analogous terminal alkenes:




**Scheme 1**

Scheme 1 shows how OH radicals are produced from long-chain terminal alkene ozonolysis. Terminal alkenes such as 1-hexene, 1-heptene and 1-octene have overall OH yields from ozonolysis of ~0.33.[53-54] These compounds are known to produce $CH_2OO$ in a molar yield ($x_{CH_2OO}$) of ~0.5 [53]. The OH yield of $CH_2OO$ produced through ozonolysis has been determined to be 0.16.[53] Rickard et al.[54] recommend that *syn*-CIs have a unit OH yield whereas *anti*-CIs do not yield OH, and the overall OH yield can therefore be described as follows:

$$1.0 \cdot x_{syn} + \left(0.16 \cdot x_{CH_2OO}\right) = 0.33 \text{ (VII)}$$

which gives a value for $x_{syn}$ of 0.25. Since the three possible CIs formed must sum to a yield of one, the yield of *anti*-CI ($x_{anti}$) will be 0.25 also.

The third assumption is that the ratio of rate coefficients for *syn*- and *anti*-$C_{13}H_{26}OO$ is similar to that for the *k* $(CH_3)_2COO$ and $CH_2OO + CH_3OH$ measured in this study (0.42 at 298 K); in the case of $(CH_3)_2COO$, the terminal oxygen atom always faces towards an alkyl substitution and is considered to be representative of a purely *syn*-CI, whereas $CH_2OO$ never faces an alkyl substitution and is considered to be purely *anti* in character. Since the relative rate coefficient of Tobias and Ziemann[20] only considers the fate of the $C_{13}H_{26}OO$ CIs, the above values of 0.25 are effectively doubled, and by accounting for the ratio of $k_1$ and $k_3$ from this study, Eq. VI is simplified as follows:

$$\frac{k_{anti} \cdot 0.71}{1 \times 10^{-10}} = 0.0013 \text{ (VIII)}$$

from which individual rate coefficient values of $2 \times 10^{-13}$ and $8 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ can be obtained for *anti*- and *syn*-$C_{13}H_{26}OO$ respectively. These values are a factor of 2 larger than the rate coefficients determined in this work. Given that at least some of these differences may be physical between the $C_{13}$ CIs and the smaller CIs that have been studied here, and assuming that no major

cancellation of errors results from the above assumptions, the level of agreement is satisfactory. This comparison suggests that the static chamber ozonolysis experiments, if conducted under the right conditions, are a reliable source of kinetic data for the reactions of large CIs that cannot be accessed through the direct methodology employed in this work.

## 7. Conclusions

Direct experimental rate coefficient measurements for the reactions of $CH_2OO$ and $(CH_3)_2COO$ + methanol and that of $CH_2OO$ + ethanol are presented. Experimental conditions were varied between temperatures of 254 and 329 K, and pressures of 10 and 100 Torr ($N_2$), with no evidence of pressure dependence and a strong non-Arrhenius temperature dependence observed in all cases. The rate coefficient of $(CH_3)_2COO$ + methanol exhibited both a negative and positive temperature-dependent component, which may in part be explained by a higher barrier encountered by the pre-reactive complex as it proceeds to product formation. It is acknowledged, however, that this alone is insufficient to explain the extent of the temperature dependence observed, and a more rigorous theoretical treatment is required. The insertion reactions by which CIs react with alcohols produce $\alpha$-alkoxyalkyl hydroperoxides (AAAHs). The calculated UV cross section of a representative of these species, methoxymethyl hydroperoxide (MMHP), is found to be similar to other peroxides, indicating that whilst tropospheric photolysis is an important sink for these species, oxidation and deposition are likely to be competitive. Based on these findings, a global chemistry transport model is used to estimate the abundance and flux of AAAHs into the global atmosphere. A total flux of ~30 Gg $Yr^{-1}$ is obtained, with most production occurring in the tropical forests, where biogenic methanol and alkene emissions are both high.

## Supporting Information

Tabulated experimental data and conditions. Computational details for UV cross section and potential energy calculations. Kinetic parameters employed in atmospheric chemical modelling. NMR spectra for $(CH_3)_2CI_2$ sample. Kinetic analysis of experimental observations.

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