Chhantyal Pun, R., Khan, M. A. H., Zachhuber, N., Percival, C., Shallcross, D. E., & Orr-Ewing, A. J. (2020). Impact of Criegee Intermediate Reactions with Peroxy Radicals on Tropospheric Organic Aerosol. *ACS Earth and Space Chemistry*, 4, 1743-1755. [10].
<https://doi.org/10.1021/acsearthspacechem.0c00147>

Peer reviewed version

Link to published version (if available):
[10.1021/acsearthspacechem.0c00147](https://doi.org/10.1021/acsearthspacechem.0c00147)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via American Chemical Society at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.0c00147> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

Impact of Criegee Intermediate Reactions with Peroxy Radicals on Tropospheric Organic Aerosol

Rabi Chhantyal-Pun,^{1} M. Anwar H. Khan,¹ Nicholas Zachhuber,¹ Carl J. Percival,² Dudley E. Shallcross,¹ and Andrew J. Orr-Ewing¹*

¹School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom, ²Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Drive, Pasadena, California 91109-8099, United States

KEYWORDS. Atmospheric Chemistry, Criegee Intermediates, Peroxy Radicals, Radical Reactions, Secondary Organic Aerosol, Cavity Ring-Down Spectroscopy, Chemical Transport Modelling

ABSTRACT. Peroxy radicals and carbonyl oxides (Criegee intermediates) are produced in the troposphere during OH and ozone-initiated oxidation of hydrocarbons. Reactions between these species have previously been shown to form highly oxidized molecules which can condense to form secondary organic aerosols. Here, cavity ring-down spectroscopy coupled with laser flash photolysis was used to measure directly rate coefficients for reactions of CH₂OO with CH₃O₂ and CH₃C(O)O₂. The rate coefficients were found to be similar within the measurement uncertainties and only weakly dependent on temperature (in the range 243 – 310 K) and pressure (10 - 100 Torr, N₂). A combined rate coefficient of $k(\text{CH}_2\text{OO}+\text{RO}_2, \text{RO}_2 = \text{CH}_3\text{O}_2/\text{CH}_3\text{C}(\text{O})\text{O}_2) = (2.4 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained under these conditions. Global modelling

using STOCHEM-CRI, updated with monoterpene chemistry generating Criegee intermediates, and supplemented by regional box modelling, shows that this class of Criegee intermediate + peroxy radical reactions can contribute up to ~1.3% of secondary organic aerosol production in forested regions of the world.

Introduction

Peroxy radicals, RO_2 , are important intermediates in the troposphere, directly affecting NO_x and ozone concentrations.¹ Methyl peroxy, CH_3O_2 , is the simplest and the most abundant organic peroxy radical and is produced during OH radical initiated oxidation of methane.^{2, 3} Acyl peroxy radicals like acetyl peroxy, $\text{CH}_3\text{C}(\text{O})\text{O}_2$, can combine with NO_2 to form peroxyacyl nitrates (PAN) which facilitate long range transport of NO_x .⁴ Carbonyl oxides, commonly referred to as Criegee intermediates, are produced during ozonolysis of alkenes in the troposphere,⁵ and are potentially important oxidants in the forested regions of the world.⁶⁻⁸ The simplest Criegee intermediate, formaldehyde oxide (CH_2OO) reacts mainly with H_2O dimer in the troposphere,^{9, 10} but larger biogenic Criegee intermediates can react with other trace tropospheric species like NO_2 , SO_2 , carboxylic acids, HNO_3 and HCl .^{11, 12}

Atmospheric simulation chamber and flow reactor measurements by Zhao et al. using mass spectrometric detection have shown that Criegee intermediates from the ozonolysis of trans-3-hexene undergo oligomerization reactions with RO_2 to produce adducts with several Criegee intermediate chain units.¹³ These oligomers were found to have high molecular weights and contribute to particle growth and new particle formation in their experiments. Sadezky et al. proposed peroxy radical – Criegee intermediate reactions to explain oligomers with chain units

corresponding to the Criegee intermediate mass in the secondary organic aerosols (SOAs) produced during ozonolysis of ethyl butenyl ether, *trans*-3-hexene, 2,3-dimethyl-2-butene and *trans*-4-octene in a glass reactor.¹⁴ Sakamoto et al. also observed oligomerization products in the SOA formed during ozonolysis of ethene in a Teflon chamber, but proposed reaction of Criegee intermediates with hydroperoxides.¹⁵ Quantum Chemistry calculations using single reference and multiconfiguration methods have predicted formation of a stable association product through a submerged barrier for the reaction of CH₂OO with CH₃O₂, suggesting a fast reaction rate.¹⁶⁻¹⁸ However, significant uncertainty remains in quantifying the effect of these reactions in the troposphere because accurate rate coefficients have not been available.

Here we present the first direct experimental study of this class of reactions, conducted in a flow cell using laser flash photolysis to produce CH₂OO and RO₂, and cavity ring-down spectroscopy (CRDS) to monitor the rate of loss of CH₂OO. A chemical reaction scheme, used previously to estimate global Criegee intermediate concentrations,¹⁹ has been updated to provide improved estimates for the concentrations of monoterpene derived Criegee intermediates. The experimental measurements, along with the updated reaction scheme in a chemical transport model, STOCHEM-CRI, are used to assess the impact of reactions of RO₂ radicals with Criegee intermediates on tropospheric organic aerosol production.

Methods

Cavity Ring-down Spectroscopy

The CRDS apparatus, coupled with a variable temperature flow cell, has been described in detail in our previous publications.²⁰⁻²² Briefly, CH₂OO was produced by 266 nm laser photolysis of CH₂I₂ in the presence of O₂ as described previously by Taatjes and co-workers.²³ CH₃O₂ and

CH₃C(O)O₂ were both produced by 266 nm photolysis of acetone in the presence of O₂. CH₃I photolysis was not used because this method produces additional I atoms which can interfere with the CH₂OO kinetics. CH₂I₂, O₂, NO, and (CH₃)₂CO partial pressures of around 0.001, 5, 0.018 and 0.05-0.25 Torr were used for various experiments, with the balance pressure provided by N₂. The photolysis radiation was generated using the fourth harmonic of a Nd:YAG (Continuum Surelite I) laser. The probe radiation at 355 nm was produced by doubling the visible output of a dye laser (pyridine I) pumped by the second harmonic of a Nd:YAG (Continuum Surelite II) laser. The timings of the two lasers were controlled by a pulse generator. A custom written LabView virtual instrument automated the change in time delay between the two lasers, and performed ring-down fitting as well as background subtraction upon photolysis at each time delay. The measured change in the ringdown rate upon photolysis is directly related to the concentration of absorbing species:

$$N(t) = \frac{\Delta\kappa(t) L}{cd\sigma_{355nm}} \quad (E1)$$

Here, $\Delta\kappa$ is the change in ringdown rate upon photolysis, $L = 106$ cm is the length of the cavity, c is the speed of light, $d = 7.6$ cm is the photolysis and probe laser overlap length and σ_{355nm} is the absorption cross section of either CH₂OO (1.1×10^{-17} cm² molecule⁻¹)²⁴ or NO₂ (4.755×10^{-19} cm² molecule⁻¹)²⁵ at the 355 nm probe wavelength. The jacketed flow cell used for the temperature dependent kinetic experiments had a coolant circulating around the laser overlap region. The low temperature limit (243 K) of the experiments was imposed by the vapour pressure of the CH₂I₂ precursor. Numerical modelling and fits were performed for the kinetic traces using custom-written Python scripts. The SciPy (odeint) and LMFIT modules of Python were used for numerical integrations and least squares fitting, respectively.

Chemical Transport Modelling

A global chemical transport model, STOCHEM, was used to assess the tropospheric impact of the reaction between Criegee intermediates and peroxy radicals. STOCHEM is a 3-dimensional tropospheric chemistry and transport model which is based on a Lagrangian approach. This approach uses 50,000 air parcels which are advected by winds generated from the UK Meteorological office global circulation model with a 3h timestep.²⁶ It is an offline model with the radiation codes and transport driven by archived meteorological data provided by the UKMO Unified Model (UM) at a grid resolution of 1.25° longitude, 0.8333° latitude and 12 unevenly spaced vertical levels with an upper boundary of 100 hPa.²⁷

The emissions data of CO, NO_x and non-methane volatile organic compounds (VOCs) used in the STOCHEM model were adapted from the Precursor of Ozone and their Effects in the Troposphere (POET) inventory.²⁸ The total emissions of CH₄ were obtained from Mikaloff-Fletcher et al.²⁹ except the oceanic emissions, which were taken from Houweling et al.³⁰ The surface emissions from anthropogenic sources, biomass burning, oceans and soils were added using monthly 2-D source maps at a resolution of 5° × 5°.³¹ The vegetation emission used in the model was based on the vegetation distribution of Cox et al.³² and algorithms of Guenther et al.³³ Isoprene is emitted during the day but has no emissions at night, so the emission rate of isoprene in the model was adjusted with consideration of the solar zenith angle. The emission rate was also adjusted monthly to account for the number of daylight hours in a given region over the year. The isoprene emissions of 501 Tg/yr and monoterpenes emissions of 162 Tg/yr used in the model were based on the Guenther et al. study.³⁴

The chemical mechanism used in STOCHEM is the ‘Common Representative Intermediates mechanism version 2 and reduction 5’ (CRI v2-R5). CRI v2-R5 was developed using the Master Chemical Mechanism version 3.1 (MCM 3.1), reducing the number of species and reactions by 90%, with ozone production being the primary criterion.³⁵ More details about the development of CRI v2-R5 can be found in References 35-37 with updates of the SOA module described in References 38, 39 and isoprene HO_x recycling highlighted by Jenkin et al.⁴⁰ A further addition of the Criegee field into the CRI by Chhantyal-Pun et al.¹⁹ involved the inclusion of 17 individual stabilized Criegee intermediates (SCIs) along with explicit formation from ozonolysis reactions of alkenes and loss processes by unimolecular decomposition, and/or reaction with water and water dimer.

Results and Discussion

R=(CH₃+CH₃C(O)) Concentration Calibration

In our kinetic experiments, the initial concentrations of CH₃ and CH₃C(O) radicals in the flow cell were determined by subsequent reactions with O₂ to produce CH₃O₂ and CH₃C(O)O₂ which were then titrated with NO to produce NO₂ (R24 and R25, with rate coefficient units for these and all other bimolecular reactions in our schemes of cm³ molecule⁻¹ s⁻¹). Figure 1 shows NO₂ concentrations measured as a function of time delay between the photolysis and probe lasers. There is an initial rapid rise due to reaction of NO with CH₃O₂ and CH₃C(O)O₂ and a slow decay at longer time because of reactive and physical losses. The NO₂ kinetic traces were fitted using the least squares method to a numerical model which included reactions R2-R39, and the results are shown in Figure 1. The temperature dependent rate coefficients for these reactions were

obtained from the IUPAC gas kinetic database.⁴¹ The initial concentrations of CH₃ and CH₃C(O) radicals and rate coefficient for the slow decay process, R39, were varied in the fits. The quantum yields of CH₃ ($\phi_{\text{CH}_3}=1$) and CH₃C(O) ($\phi_{\text{CH}_3\text{C(O)}}=1$) in reaction R1 were taken from a previous study by Crowley and co-workers.⁴² The quantum yield values at 266 nm were not expected to be significantly dependent on pressure and temperature in the ranges studied.⁴³

The association reaction of CH₃C(O) radical with O₂ forms CH₃C(O)O₂ (R3) as well as OH (R4). The rate coefficients for these two reaction channels and their dependence on pressure and temperature were obtained from the experimental and master equation study of Carr et al.⁴⁴ The modified Troe expression from this study was used to obtain rate coefficients at various temperatures and pressures used in the current study. These values were then fitted to give Arrhenius expressions for pressures of 30 Torr ($k_3 = 4.47 \times 10^{-13} \exp(464/T)$) and 60 Torr ($k_3 = 9.75 \times 10^{-13} \exp(343/T)$) and a Lindeman expression ($6.11 \times 10^{-12} \times 3.64 \times 10^{-30} [\text{M}] / (6.11 \times 10^{-12} + 3.64 \times 10^{-30} [\text{M}]) \times 0.957$) for the N₂ bath gas pressure dependence at 293 K.

The NO₂ traces were measured at different acetone concentrations and the derived total initial radical concentrations ($R = \text{CH}_3 + \text{CH}_3\text{C(O)}$) are plotted in the inset of Figure 1. The slope of the linear fit, m , was used as a calibration to obtain total radical concentrations from (CH₃)₂CO photolysis during reaction measurements with CH₂OO. Such calibration plots were obtained separately for all the measured temperature and pressure conditions. A sensitivity analysis of m to the various rate coefficient values fixed in the numerical model shows that reactions R3, R4, R24, R25, R27 and R29 are most important. Further details of the analysis are provided in section S2 of the supporting information (SI).

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow \text{Products}$	R21, $k_{21} = 2.1 \times 10^{-12}$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{Products}$	R22, $k_{22} = 3.8 \times 10^{-12}$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow \text{Products}$	R23, $k_{23} = 5 \times 10^{-12}$
$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	R24, $k_{24} = 2.3 \times 10^{-12} \exp(360 \pm 100/T)$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{NO}_2$	R25, $k_{25} = 7.5 \times 10^{-12} \exp(290 \pm 250/T)$
$\text{CH}_3\text{O} + \text{NO} (+\text{M}) \rightarrow \text{CH}_3\text{ONO} (+\text{M})$	R26, $k_{26} = 2.6 \times 10^{-29} (T/300)^{-2.8} [\text{M}] + 2.3 \times 10^{-12} (T/300)^{-0.7}$
$\text{CH}_3\text{O}_2 + \text{NO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 (+\text{M})$	R27, $k_{27} = 2.5 \times 10^{-30} (T/300)^{-5.5} [\text{M}]$
$\text{CH}_3\text{O}_2\text{NO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2 (+\text{M})$	R28, $k_{28} = 9 \times 10^{-5} \exp(-9670/T) [\text{M}]$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 (+\text{M})$	R29, $k_{29} = 3.28 \times 10^{-28} (T/300)^{-6.87} [\text{M}]$
$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 (+\text{M}) \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 (+\text{M})$	R30, $k_{30} = 1.1 \times 10^{-5} \exp(-10100/T) [\text{M}]$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O} + \text{NO}_2$	R31, $k_{31} = 8 \times 10^{-12}$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2\text{NO}_2$	R32, $k_{32} = 6.4 \times 10^{-12}$
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2\text{NO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 + \text{NO}_2$	R33, $k_{33} = 1.4 \times 10^{16} \exp(-10730/T)$
$\text{OH} + \text{NO} (+\text{M}) \rightarrow \text{HONO} (+\text{M})$	R34, $k_{34} = 7.4 \times 10^{-31} (T/300)^{-2.4} [\text{M}]$
$\text{OH} + \text{NO}_2 (+\text{M}) \rightarrow \text{HONO}_2 (+\text{M})$	R35, $k_{35} = 3.2 \times 10^{-30} (T/300)^{-4.5} [\text{M}]$
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	R36, $k_{36} = 3.45 \times 10^{-12} \exp(270/T)$
$\text{HO}_2 + \text{NO}_2 (+\text{M}) \rightarrow \text{HO}_2\text{NO}_2 (+\text{M})$	R37, $k_{37} = 1.4 \times 10^{-31} \exp(T/300)^{-3.1} [\text{M}]$
$\text{HO}_2\text{NO}_2 (+\text{M}) \rightarrow \text{HO}_2 + \text{NO}_2 (+\text{M})$	R38, $k_{38} = 4.1 \times 10^{-5} \exp(-10650/T) [\text{M}]$
$\text{NO}_2 \rightarrow \text{Sink}$	R39, $k_{39} (\text{varied})$

Figure 1. Representative NO_2 kinetic traces obtained from reactions of RO_2 radicals with NO at 60 Torr and 243 K. Each trace corresponds to a different starting concentration of the RO_2 precursor, acetone. Traces are taken at high- and low-resolution time steps to capture the initial rapid rise as well as slower decay processes. The dashed lines show the numerical fits obtained using the reaction scheme described in the text. The inset shows the derived total radical concentration ($\text{R}=\text{CH}_3+\text{CH}_3\text{C}(\text{O})$) plotted as a function of acetone concentration (both specified in units of molecule cm^{-3}) and a linear fit.

Spectral Interference Subtraction

Figure 2 shows the CRDS signal at 355 nm obtained during $\text{CH}_2\text{OO} + \text{RO}_2$ reaction measurements. The dominant contributor to the absorption at 355 nm is CH_2OO which can be titrated completely by reaction with added trifluoroacetic acid (TFA) as shown by the green trace for measurements made in the absence of peroxy radicals. The reaction of CH_2OO with TFA is fast and produces an adduct which does not absorb in this region.^{7, 21} The red trace shows the 355

nm absorption signal in the presence of CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$, produced by photolysis of $(\text{CH}_3)_2\text{CO}$. Contrary to our previous measurements for the $\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{CO}$ reaction, using 355 nm photolysis instead of the 266 nm used here,¹⁹ the CRDS signal does not completely decay away even at long photolysis-probe laser delay. Moreover, when TFA is introduced into the reaction system, there is a non-zero signal which matches the magnitude of the persistent signal from the $\text{CH}_2\text{OO} + \text{RO}_2$ reaction measurement. This shows that the persistent signal is independent of CH_2OO , but dependent on the 266-nm photolysis laser. Photolysis of either $(\text{CH}_3)_2\text{CO}$ or CH_2I_2 separately does not give any such absorption signal at 355 nm. Thus, the signal must arise from reaction between photolysis products of $(\text{CH}_3)_2\text{CO}$ and CH_2I_2 . Previously, reaction between I and CH_3O_2 has been shown to produce CH_3OOI which absorbs in the near UV region and is likely to be responsible for this signal.⁴⁵ The background traces obtained with added TFA were therefore subtracted from the $\text{CH}_2\text{OO} + \text{RO}_2$ traces to remove this contribution to the measurements, giving an interference free CH_2OO kinetic decay trace for all the measurements performed in this study. The concentrations of CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ are always in excess of the I atom concentration for the experimental conditions used and thus this side reaction should not significantly affect the initial RO_2 concentration.

Figure 2. Spectral interference subtraction to obtain a CH₂OO absorption signal at 355 nm probe wavelength. The ordinate shows the change in ring down rate constant upon photolysis of the gas mixture, which is directly proportional to total concentration of the absorbing species. The red, blue and green traces show kinetic profiles in the presence of the species labelled in the legend. TFA stands for trifluoroacetic acid. (CH₃)₂CO is used as a precursor for RO₂ (CH₃O₂ and CH₃C(O)O₂) as described in the main text.

CH₂OO + RO₂ Reaction Kinetics

Figure 3 shows an example of a background subtracted CH₂OO absorption decay trace obtained in the presence of RO₂ radicals. This and other CH₂OO kinetic decay traces were fitted using the least squares method to a numerical model which included reactions R2-R23 and R40-R46. The rate coefficients for self-reaction, R40, and unimolecular reactions, R41, of CH₂OO were obtained from separate fits to CH₂OO decay traces obtained in the absence of co-reactants (see section S1 of the SI). These latter measurements and fits were performed for all the different pressure and temperature conditions used for the CH₂OO + RO₂ studies to establish the T and p-

dependence of the R40 and R41 rate coefficients. The temperature dependent rate coefficient expressions for reactions R42 and R44 were obtained from our recent studies.^{19, 46} The reaction of CH₂OO with CH₃COOH, R43, is near the collision limit,^{7, 47} and analogous to the reaction of CH₂OO with CF₃COOH, the rate coefficient value was not expected to vary significantly with temperature.²¹ A sensitivity analysis of the fit model is presented in section S2 of the SI.

In general, the reactions of CH₃C(O)O₂ are faster than those of CH₃O₂, e.g. the CH₃C(O)O₂ self-reaction rate coefficient is greater by 3 orders of magnitude, and the rate coefficient for reaction with NO is greater by an order of magnitude.⁴¹ Thus, in initial fits, the values of k_{45} and k_{46} , constrained to satisfy $k_{45} \leq k_{46}$, were varied. However, the two-rate coefficient values obtained were similar within the uncertainty of the fits, as shown in Figure S2 of the SI. Thus, k_{45} and k_{46} , labelled k_{RO_2} , were constrained to be equal in all the subsequent fits performed for temperature and pressure dependent measurements.

The initial concentrations of CH₃ and CH₃C(O) radicals were obtained from calibration curves of the type shown in Figure 1. Figure 3 also shows the CH₂OO fitted trace and the modelled concentrations of CH₃O₂, CH₃C(O)O₂, CH₃COOH, CH₃OH, HO₂ and CH₃C(O)CH₂O₂ obtained using the optimised parameters from the fit. At least three CH₂OO decay traces were measured at different concentrations of acetone for each set of pressure and temperature conditions, and the resulting rate coefficient values were averaged. A detailed analysis of possible systematic errors arising from variation of the quantum yield for R1, the photolysis-probe laser overlap length, variation in rate coefficients fixed in the fit model, and exclusion of other possible reactions in the fit model is provided in section S2 of the SI.

$\text{CH}_2\text{OO} \rightarrow \text{Product2}$	R41, k_{uni} (see text)
$\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{CO} \rightarrow \text{Ozonide}$	R42, $k_{42} = (1.4 \pm 0.2) \times 10^{-21} \text{ T}^2 \exp(2421 \pm 40/T)$
$\text{CH}_2\text{OO} + \text{CH}_3\text{COOH} \rightarrow \text{Product5}$	R43, $k_{43} = (1.5 \pm 0.1) \times 10^{-10}$
$\text{CH}_2\text{OO} + \text{CH}_3\text{OH} \rightarrow \text{Product6}$	R44, $k_{44} = (3.7 \pm 1.4) \times 10^{-21} \text{ T}^2 \exp(1710 \pm 103/T)$
$\text{CH}_2\text{OO} + \text{CH}_3\text{O}_2 \rightarrow \text{Product3}$	R45, k_{45} ($k_{45} = k_{46}$, varied)
$\text{CH}_2\text{OO} + \text{CH}_3\text{C(O)O}_2 \rightarrow \text{Product4}$	R46, k_{46} ($k_{45} = k_{46}$, varied)

Figure 3. Measurement and model fitting for reactions of CH_2OO with CH_3O_2 and $\text{CH}_3\text{C(O)O}_2$.

The lighter grey solid trace in the top panel shows the experimental CH_2OO concentration measurement obtained in the presence of CH_3O_2 and $\text{CH}_3\text{C(O)O}_2$ at 60 Torr and 243 K. The solid red line is a fit obtained using the numerical model described in the text, with residuals shown in the bottom panel. The dashed lines with different symbols show the modelled concentrations of various species, obtained using optimised parameters from the fit. Note that the

CH₃ radical is recycled rapidly from reaction R7 leading to a slight increase in the concentration of CH₃O₂ at early photolysis-probe delay times.

Figure 4 shows the measured rate coefficients for the reaction of CH₂OO with CH₃O₂ and CH₃C(O)O₂ at different total pressures in the flow cell and at room temperature (293 K). The total pressure was raised by increasing the flow rate of N₂ while keeping the flow rates of other gases constant. The derived rate coefficients are only weakly dependent on pressure and are within the measurement uncertainties in the 20 to 100 Torr range. A pressure independent value, $k_{\text{RO}_2} = (2.4 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was obtained by averaging the values shown in Figure 4 and taking the 2 σ value as the error estimate.

Figure 4. Pressure dependence of the rate coefficients for the reaction of CH₂OO with CH₃O₂ and CH₃C(O)O₂ at 293 K. The error bars show a combination of statistical errors from the fit and systematic errors as described in the SI.

Figure 5 shows the temperature dependence of the rate coefficients for reaction of CH₂OO with CH₃O₂ and CH₃C(O)O₂ radicals, obtained at 30 and 60 Torr total pressures. The rate coefficient

values show only a weak temperature dependence and are within the measurement uncertainties in the 243-310 K range. A temperature independent value, $k_{\text{RO}_2} = (2.4 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained by averaging the values shown in Figure 5 and taking the 2σ value as the error estimate. Thus, a rate coefficient value of $(2.4 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is derived as the best estimate for the reaction of CH_2OO with CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ under a 10 to 100 Torr (N_2) pressure range and a 243 to 310 K temperature range.

Figure 5. Temperature dependence of rate coefficients for the reactions of CH_2OO with CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$. The rate coefficient values were measured at 30 (open circle) and 60 Torr (filled circle) total pressures as described in the SI. The error bars incorporate a combination of statistical errors from the fit and systematic errors as described in the text.

The order of magnitude of the rate coefficient value, $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for the reaction of CH_2OO with CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is consistent with a barrierless addition mechanism

predicted by previous computational studies.¹⁶⁻¹⁸ Considering that the reactive pathway involves the peroxy radical attacking the carbonyl carbon of the Criegee intermediates, the orientation of the $\text{C}=\text{O}^+-\text{O}^-$ moiety which results in various conformeric forms of larger Criegee intermediates is not expected to change significantly the reaction rate. Observation by Zhao et al. and Sadezky et al. of Criegee intermediate reactions with peroxy radicals during the ozonolysis of various alkenes also suggests that the feasibility of this class of reactions is not adversely affected by an increase in the structural complexity of the Criegee intermediates and peroxy radical reaction partners.^{13, 14} Berndt et al. showed that the reaction of larger Criegee intermediates, such as those derived from cyclohexene, may be significantly slower than the simpler Criegee intermediates because of intramolecular attraction between the carbonyl oxygen (at the aldehyde end) and the zwitterionic carbon located at the two ends of the Criegee intermediate.⁴⁸ Thus, larger Criegee intermediates derived from sesquiterpenes may have significantly slower reaction rate coefficients. None of the Criegee intermediates, as shown in Table 1 and used in the model calculations described later, were expected to have similarly strong intramolecular interactions.

Global Gas Phase Modelling

Global modelling was performed using STOCHEM-CRI to assess the impact of Criegee intermediate reactions with RO_2 radicals in the troposphere. The Criegee intermediate field in STOCHEM-CRI model developed by Chhantyal-Pun et al. was used with updates for the monoterpene derived Criegee intermediates.¹⁹ Previously, emissions of σ - and β -pinenes were scaled to account for all the monoterpenes and simplify the chemical scheme in the CRI. Here, the ozonolysis chemistries of various monoterpenes were explicitly included using an updated emissions inventory and rate coefficients for ozonolysis and Criegee intermediate reactions. The

emissions inventory reported by Sindelarova et al. for various monoterpenes (σ -pinene, β -pinene, limonene, ocimene, myrcene, sabinene, carene) was used in this study.⁴⁹

The updated yield values for SCIs from ozonolysis reactions and the rate coefficients for the dominant loss reactions used in the model are provided in Table 1. Only the total SCI yield values are available for most ozonolysis reactions and were divided equally among various SCI isomers and conformers. For β -pinene, the yield value for C9 SCI, divided equally among two conformers, was taken from the theoretical study of Nguyen et al.⁵⁰ which is in good agreement with experimental studies of Ahrens et al. and Winterhalter et al.^{51, 52} The CH₂OO yield value varies from 0.05 to 0.16 in these studies and a value of 0.15 was used as recommended by IUPAC.⁵³ The total SCI yield from ozonolysis of limonene was obtained from averaging values obtained by Newland et al. and Sipilia et al.^{54, 55} SCI yield values for ozonolysis reactions of carene and sabinene are not available in the literature and thus the yield values for σ - and β -pinenes were used based on their structural similarities. For limonene, the ozonolysis reaction has been shown to proceed mostly through addition to the endocyclic double bond,⁵⁶ and the SCI yield value was divided evenly among the four possible resulting SCIs. For ocimene and myrcene, a previous study by Reissell et al. suggested that the ozonolysis reaction mainly proceeds by adding to the CH=C(CH₃)₂ bond and thus the total SCI yield values were divided evenly among (CH₃)₂COO and two conformers of 4-vinyl (3 or 4)-pentanaldehyde oxides.⁵⁷

Table 1. Criegee intermediates generated during ozonolysis of various monoterpenes. The rate coefficients for unimolecular and bimolecular reactions with H₂O/(H₂O)₂ are provided in s⁻¹ and cm³ molecule⁻¹ s⁻¹ units, respectively. Percent contributions of each Criegee intermediate in terms of number and mass concentrations (in parentheses) are also provided.

Criegee Intermediate	Alkene (SCI yield)	Loss rate coefficients	Percent Contribution
CH ₂ OO	Sabinene (0.15) β -Pinene (0.15)	$k_{(\text{H}_2\text{O})_2} = 3.92 \times 10^{-16} \exp(2930/T)$ $k_{(\text{H}_2\text{O})_2}(298) = 7.3 \times 10^{-12}$ [Ref ⁹]	0.32 (0.09)

<p>ACETOO</p>	0.15 (Ocimene) 0.15(Myrcene)	$k_{\text{uni}}=4.83 \times 10^{-74} T^{28.6} \exp(3426/T)$ $k_{\text{uni}}(298) = 275$ [Ref ⁵⁸]	27 (12)
<p>NOPINOO-I</p>	0.18 (β -Pinene) [Ref ⁵⁰⁻⁵²]	$k_{\text{uni}}=2.76 \times 10^{-73} T^{27.88} \exp(3978/T)$ $k_{\text{uni}}(298) = 166$ [Same as <i>syn</i> -CH ₃ CHOO, Ref ⁵⁹]	1.7 (1.6)
<p>NOPINOO-II</p>	0.18 (β -Pinene)	$k_{\text{uni}}=1.9 \times 10^9 T^{1.33} \exp(-8425/T)$ $k_{\text{uni}}(298) = 2$ $k_{\text{H}_2\text{O}}=8.46 \times 10^{-23} T^{2.64} \exp(121/T)$ $k_{\text{H}_2\text{O}}(298) = 4.3 \times 10^{-16}$ [Ref ⁶⁰]	1.6 (1.5)
<p>SABINOO-I</p>	0.18 (Sabinene) [same as β -pinene]	[Same as <i>syn</i> -CH ₃ CHOO and NOPINOO-I]	1.8 (1.7)
<p>SABINOO-II</p>	0.18 (Sabinene)	[Same as NOPINOO-II]	1.9 (1.8)
<p>PINONOO-I</p>	0.05 (σ -pinene) [Ref ^{55, 61}]	$k_{\text{H}_2\text{O}}= 1.3 \times 10^{-14}$ $k_{(\text{H}_2\text{O})_2}=5.23 \times 10^{-20} \exp(6124/T)$ $k_{(\text{H}_2\text{O})_2}(298) = 4.4 \times 10^{-11}$ [Same as <i>anti</i> -CH ₃ CHOO, Ref ⁶²]	0.03 (0.03)
<p>PINONOO-II</p>	0.05 (σ -pinene)	$k_{\text{uni}}=3.59 \times 10^{-70} T^{26.8} \exp(3815/T)$ $k_{\text{uni}}(298) = 265$ [Same as <i>syn</i> -CH ₃ CH ₂ CHOO, Ref ⁶³]	3.0 (3.4)
<p>sPINONOO-I</p>	0.05 (σ -pinene)	[Same as ACETOO]	10 (12)
<p>sPINONOO-II</p>	0.05 (σ -pinene)	$k_{\text{uni}}=6.95 \times 10^{-66} T^{25.7} \exp(2391/T)$ $k_{\text{uni}}(298) = 82$ [Ref ⁶⁰]	3.1 (3.5)

<p>sCARENOO-I</p>	0.05 (3-Carene) [same as σ -pinene]	[Same as ACETOO]	0.34 (0.38)
<p>sCARENOO-II</p>	0.05 (3-Carene)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	0.34 (0.38)
<p>CARENOO-I</p>	0.05 (3-Carene)	[Same as <i>anti</i> - CH ₃ CHOO]	0 (0)
<p>CARENOO-II</p>	0.05 (3-Carene)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	0.34 (0.38)
<p>LIMONOO-I</p>	Limonene (0.06) [Ref ^{54, 55}]	[Same as <i>anti</i> - CH ₃ CHOO]	0.02 (0.02)
<p>LIMONOO-II</p>	Limonene (0.06)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	2.1 (2.4)
<p>sLIMONOO-I</p>	Limonene (0.06)	[Same as ACETOO]	2.1 (2.4)
<p>sLIMONOO-II</p>	Limonene (0.06)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	2.1 (2.4)
<p>OCIMENOO-I</p>	0.075 (Ocimene) [Ref ⁵⁴]	[Same as <i>anti</i> - CH ₃ CHOO]	0.12 (0.10)

OCIMENOO-II	0.075(Ocimene)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	12 (9.0)
MYRCENOO-I	0.075(Myrcene) [Ref ⁵⁴]	[Same as <i>anti</i> -CH ₃ CHOO]	0.02 (0.02)
MYRCENOO-II	0.075(Myrcene)	[Same as <i>syn</i> -CH ₃ CH ₂ CHOO]	2.1 (1.7)

Table 1 lists the best rate coefficient estimates for reactions of monoterpene derived SCIs, based on structural similarity with smaller SCIs for which directly measured rate coefficients are now available. The main loss processes for SCI in the troposphere are unimolecular decomposition or reaction with water, hence Table 1 focuses on these pathways. The magnitudes of these two loss processes depend on the structure of the SCI, with the *anti*- conformers (I) predominantly reacting with water, whereas the *syn*- conformers (II) undergo unimolecular decomposition.^{12, 60} Here, the *syn*- conformers are taken as structures with the SCI terminal oxygen pointing towards the more substituted α - carbon and vice versa for the *anti*- conformers. Also, the SCIs with the carbonyl group connected to the zwitterionic secondary carbon, denoted by ‘s’ in the labels, were expected to only undergo unimolecular decomposition reactions. The rate coefficients for *syn*-CH₃CHOO, *syn*-CH₃CH₂CHOO, *anti*-CH₃CHOO and (CH₃)₂COO, which are relatively well studied by direct methods, were used based on structural similarities with the SCIs shown in Table 1. For most of the *syn*- conformers, the unimolecular decomposition rate coefficient of *syn*-CH₃CH₂CHOO was used instead of *syn*-CH₃CHOO to account for the presence of a second conformer upon rotation of the α - carbon. For NOPINOO-I, this is not possible and the rate coefficient of *syn*-CH₃CHOO was used instead.

Figure 6. Global surface concentration of stabilized Criegee intermediates generated from ozonolysis of a) monoterpenes and b) all alkenes. The plot shows concentrations averaged over the months of June, July and August.

Figure 6a shows the global concentrations of SCI generated from ozonolysis of monoterpenes. Highest concentrations of around 2000 molecule cm⁻³ are estimated in the Amazon region, which is 3× times higher than our previously estimated values for monoterpene derived SCIs.¹⁹ This estimate is lower by around an order of magnitude than the estimates of Newland et al.⁵⁴ Using

their chemical reaction scheme, our model predicted concentrations similar to our estimates, suggesting that the concentrations differences between the two studies may arise from OH radical chemistry. The CRI version used here has been recently updated with OH radical recycling isoprene chemistry and has higher OH radical concentrations in low NO_x environments (e.g. the Amazon),⁴⁰ leading to lower branching towards ozonolysis during the initial oxidation of monoterpenes.

Figure 6b shows the updated sum of Criegee intermediates derived from monoterpenes, as well as from simpler alkenes such as ethene, propene, *E*-2-butene, isoprene, methacrolein, methyl vinyl ketone and 4-hydroxy-2-methyl-2-butenal as described previously by Chhantyal-Pun et al.¹⁹ Highest concentrations of around 1×10^4 molecule cm⁻³ are estimated in the Amazon region, with the largest contribution coming from isoprene derived Criegee intermediates. However, the monoterpene derived Criegee intermediates are more evenly distributed across the globe and represent around 40% of the total global concentration. Recent field measurement by Novelli et al. estimated an average SCI concentration of 5×10^4 molecule cm⁻³ based on background OH signals in LIF-FAGE measurements.⁶⁴ Thus, the modelled SCI concentration presented here is likely to be a lower limit estimate. The rate coefficients used for Criegee intermediates derived from isoprene and other simpler alkenes are relatively well constrained by direct experimental measurements. However, the rate coefficients used for the monoterpene derived SCIs are the best available estimates as described above and will need to be refined in future, as laboratory data become available from direct methods, to provide better model estimate for SCI concentrations.

The impact of the reaction between Criegee intermediates and peroxy radicals was then modelled by adding the following chemical reactions to the CRI reaction scheme used in the global model:

Here, RO_2 and TO_2 represent a specific surrogate peroxy radical and the total combination of all surrogate peroxy radicals included in STOCHEM-CRI, respectively. The rate coefficient for reaction of CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$ with CH_2OO measured in this study was taken as the best estimate for all the reactions between peroxy radicals and Criegee intermediates. In the scheme, PO_2 represents the adduct product peroxy radical, which can react with other organoperoxy radicals (represented by TO_2), HO_2 or NO , leading to formation of alcohols (POH), organic hydroperoxides (POOH), and organic nitrates (PNO_3), respectively. The main loss processes for these secondary products are reaction with OH radicals and partitioning into an aerosol phase. The peroxy radical rate coefficients for all these reactions were taken from MCM v3.3.1 for peroxy radicals generated from α - and β - pinenes.⁵⁶

The reaction between peroxy radicals and Criegee intermediates has a relatively minor effect on the concentration of the reactants in the troposphere; however, the association products have the potential to form SOA. The combined gas phase steady state mixing ratios of the three adduct reaction products POH, POOH and PNO₃ before partitioning into the aerosol phase are shown in Figure 7. POOH and PNO₃ mixing ratios reach 1 ppt, whereas the POH mixing ratio reaches only around 0.01 ppt, and individual plots are shown in SI. The steady state approximation could not be used to estimate partitioning of the adduct products, and a separate box model was instead used as described in the next section.

Figure 7. Average surface steady state mixing ratios of adduct products (POOH, PNO₃ and POH) resulting from reactions of Criegee intermediates with peroxy radicals for the months of June, July, and August. The numbers in the boxes show secondary organic aerosol concentration (in $\mu\text{g m}^{-3}$) estimated from the box model described in the text at various locations shown by the black circles.

Secondary Organic Aerosol Box Modelling

A box model was used to estimate the partitioning of the adduct products POOH, POH and PNO₃ into the aerosol phase at various important locations around the globe. The steady state concentrations of 15 Criegee intermediates, 18 surrogate peroxy radicals, OH, NO, HO₂ and primary organic aerosols (POA) were obtained from the global model simulation for the various locations of interest. The Criegee intermediates and peroxy radicals were selected based on their potential to form SOA, which was judged either by global abundance or molecular weight. The gas phase reaction sequence M1-M7 was coupled with partitioning reactions for each of the adduct products as:

The adsorption coefficient value, $6.2 \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1} \text{ s}^{-1}$, estimated for collision of the adduct products with a monodisperse aerosol of 50 nm diameter,⁶⁵ was multiplied with POA concentrations obtained from the global model to calculate a location specific adsorption rate coefficient, k_{M8} . The desorption rate coefficient, k_{M9} , was calculated using adsorption rate and partitioning (K_p) coefficients. The partitioning coefficient was calculated using Pankow's expression and sub-cooled vapour pressures of the adduct products, as described in our previous publication.⁷ The sub-cooled vapour pressures and boiling points of POOHs were estimated using the Multiphase system online property prediction (UManSysProp) tool developed by the University of Manchester.⁶⁶ The vapour pressure and boiling point methods described by

Nannoolal et al.^{67,68} were selected for our calculations as this combination has been shown to give the best estimate for vapour pressure for various functional group compounds present in the troposphere.⁶⁹ For the same alkyl group, the vapour pressure was found to decrease as $\text{POH} > \text{PNO}_3 \gg \text{POOH}$. Some CRI peroxy radical surrogates represent more than one peroxy radical. For example, RU12OO represents 5 different peroxy radicals with two different functional groups. However, the vapour pressures of the different peroxy radicals were found to be mostly similar and the lowest estimates were used for calculations. In some cases, with significantly different vapour pressures, the overall vapour pressures were relatively large and thus the choice of vapour pressure was not critical to the partitioning calculations. A deposition lifetime of 8 days was used as a permanent sink for the SOA. The total SOA concentration from reaction of Criegee intermediates with peroxy radicals was obtained by summing SOA from condensation of PNO_3 , POOH and POH onto pre-existing POA.

Figure 8. Average northern hemisphere summer (June, July, August) speciated SOA concentrations in Brazil estimated from the box model described in the text. The ordinate and abscissa show respectively various peroxy radicals and Criegee intermediates considered in the box model. The color scale shows the SOA concentrations calculated from partitioning of the adduct products from various peroxy radical and Criegee intermediate reactions. The MCM analogues of the CRI peroxy surrogates are provided in the SI.

Figure 8 shows the estimated SOA concentrations in Brazil during June-July-August from each peroxy radical and Criegee intermediate reaction considered in the box model. Most of the SOA is produced from SCI derived from monoterpenes with only a modest contribution from smaller SCIs such as MVKOO (deriving from isoprene) which has the single largest concentration in the troposphere.¹⁹ Table 2 shows the absolute increase in SOA concentrations resulting from the reaction of Criegee intermediates with peroxy radicals, and the percent increases in SOA

concentrations at various locations compared with the background SOA in the model. Added SOA concentrations ranging from 0.001 to 0.0055 $\mu\text{g m}^{-3}$ are estimated, corresponding to an increase of 0.1 to 0.26 % at the various selected locations. POOH has the largest contribution to the SOA concentration, because of its relatively large concentration and low vapour pressures, followed by PNO_3 , whereas the POH contribution is relatively small.

The reaction of Criegee intermediates with NO_2 has been shown to follow a path similar to reaction with peroxy radicals.^{12, 70} Various direct studies have shown that the reaction rate coefficients of CH_2OO , CH_3CHOO and $(\text{CH}_3)_2\text{COO}$ Criegee intermediates with NO_2 are within a factor of 2.⁷¹⁻⁷³ Thus, an uncertainty of a factor of 2 can be taken for k_{RO_2} to account for conformational variation of the Criegee intermediates in their reactions with peroxy radicals. The SCI concentrations obtained from the global model are likely underestimated by up to a factor 5, as described above. The SOA concentration estimated from the box model increase linearly with SCI concentrations and rate coefficient value, and thus the increase in SOA concentration from the reaction of Criegee intermediates with peroxy radicals could be up to 1.3% in locations such as the Brazilian Amazon.

Table 2. SOA concentrations estimated using the box model described in the text for various locations around the globe as labelled in Figure 7. Respective contributions of POOH, PNO_3 and POH to the SOA concentrations are provided in the square brackets.

Location	Box Model SOA ($\mu\text{g m}^{-3}$)	SOA increase (%)
Amazon, Brazil	0.0055 [0.81,0.19,0.00]	0.26
Congo, Senegal	0.0040 [0.72,0.27,0.01]	0.16
Boreal, Russia	0.0030[0.74,0.26,0.00]	0.18
Georgia, USA	0.0022 [0.71,0.29,0.00]	0.08
Borneo, Malaysia	0.0010 [0.79,0.20,0.00]	0.10

A box model simulation was performed to estimate the efficiency of oligomerization reactions for addition of successive Criegee intermediate units onto peroxy radicals under typical tropospheric conditions. Using a Criegee intermediate starting concentration of 1×10^4 molecule cm^{-3} , the concentration of the peroxide product from addition of two Criegee intermediate units is around 0.005% of that of the peroxide containing just one added Criegee intermediate. This relative contribution increases to 0.025% with use of a Criegee intermediate concentration of 5×10^4 molecule cm^{-3} . Thus, only the most abundant Criegee intermediate MVKOO, produced from isoprene ozonolysis, is likely to undergo oligomerization reactions under tropospheric conditions.

A box model simulation was also performed for isoprene ozonolysis using concentrations typically found in chamber experiments.⁷⁴ The model reaction scheme is shown in the SI and includes production of Criegee intermediates along with HO_2 , OH and other subsequent reactions. OH radicals are typically scavenged by adding co-reactants such as cyclohexane to reduce the effect of OH chemistry during ozonolysis experiments. OH scavenging using cyclohexane results in production of peroxy radicals and was also included in the model. The model simulation suggests relatively high steady state concentrations of peroxy radicals ($\sim 10^{11}$ molecule cm^{-3}) and of Criegee intermediates ($\sim 10^8$ molecule cm^{-3}) are produced. The *syn*-methyl vinyl ketone oxide (*syn*-MVKOO), one of the four conformeric forms of the four-carbon Criegee intermediates from isoprene, has a slow unimolecular reaction and is unreactive towards $\text{H}_2\text{O}/(\text{H}_2\text{O})_2$.^{8, 75} Thus, *syn*-MVKOO can reach relatively large steady state concentrations and react with peroxy radicals leading to a decrease in the concentration of the Criegee intermediates by more than 30 percent. At such large concentrations, the peroxy radical adduct products could react further with Criegee intermediates, leading to formation of organic peroxides containing

multiple Criegee intermediate units, with concentrations decreasing by a factor of ~ 0.07 for each SCI addition step. Even in the absence of an OH scavenger, isoprene or other alkenes can also efficiently scavenge OH radicals to produce hydroxy substituted alkylperoxy radicals which can then react with Criegee intermediates. There is also production of peroxy radicals from decomposition of excited Criegee intermediates during ozonolysis. The reactions of isoprene and excited Criegee intermediate derived peroxy radicals are relatively complex and explicit box modelling is out of scope for this study.⁷⁶ Thus, the effect of peroxy radicals on Criegee intermediate concentrations is likely underestimated in the box model. Finlayson-Pitts and co-workers have observed oligomers with multiple SCI units during ozonolysis of *trans*-3-hexene with and without cyclohexane as an OH scavenger, suggesting the importance of this reaction pathway in static chamber as well as flow reactor experiments.¹³ Thus, the reactions of peroxy radicals with Criegee intermediates could have unintended consequences in chamber experiments.

Conclusion

The rates of reaction of Criegee intermediates with two peroxy radicals were quantified directly in laboratory experiments simulating atmospherically relevant conditions. The kinetic parameters were taken to be representative of other reactions of these two classes of reactive intermediate, and were incorporated into a global tropospheric chemistry and transport model. This model was updated with monoterpene chemistry to improve the estimation of global distributions of Criegee intermediates. The combination of the direct kinetic measurements and atmospheric modelling suggests that Criegee intermediate reactions with peroxy radicals make

non-negligible (up to a percent) contributions to SOA production in forested regions of the world. The experimental quantification of rate coefficients for examples of this important but unusual class of biradical (or zwitterionic character) intermediate + radical reactions could also be of value in interpreting oligomer and other product yields in laboratory ozonolysis experiments.

ASSOCIATED CONTENT

Supporting Information. CH₂OO Self-reaction and Unimolecular Reaction; Sensitivity Analysis; Measured Rate Coefficients; STOCHEM-CRI Global Modelling; Box Modelling

AUTHOR INFORMATION

Corresponding Author

*Rabi Chhantyal-Pun, Email: rcpchem@gmail.com, rc13564@bristol.ac.uk

Notes

The authors declare no competing financial interests.

All measured CRDS data and python script for SOA box modelling are archived in the University of Bristol's Research Data Storage Facility (DOI: 10.5523/bris.8b698k3w002o2sxke19jc2mux).

ACKNOWLEDGMENT

This research was funded by the Natural Environment Research Council (NERC, grants NE/K004905/1 and NE/P013104/1). The authors thank Drs. Craig Taatjes, Rebecca Caravan and Mike Jenkin for helpful discussions. CJP's work was carried out at Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), and was supported by the Upper Atmosphere Research and Tropospheric Chemistry Programs.

REFERENCES

1. Derwent, R. G.; Jenkin, M. E.; Saunders, S. M., Photochemical Ozone Creation Potentials for a Large Number of Reactive Hydrocarbons under European Conditions. *Atmos. Environ.* **1996**, *30*, 181-199.
2. Khan, M. A. H.; Cooke, M. C.; Utembe, S. R.; Archibald, A. T.; Derwent, R. G.; Jenkin, M. E.; Morris, W. C.; South, N.; Hansen, J. C.; Francisco, J. S.; Percival, C. J.; Shallcross, D. E., Global Analysis of Peroxy Radicals and Peroxy Radical-Water Complexation using the STOCHEM-CRI Global Chemistry and Transport Model. *Atmos. Environ.* **2015**, *2015*, 278-287.
3. Calvert, J. G.; Derwent, R. G.; Orlando, J. J.; Tyndall, G. S.; Wallington, T. J., *Mechanisms of Atmospheric Oxidation of the Alkanes*. Oxford University Press: New York, USA, 2008; p 174-204.
4. Fischer, E. V.; Jacob, D. J.; Yantosca, R. M.; Sulprizio, M. P.; Millet, D. B.; Mao, J.; Paulot, F.; Singh, H. B.; Roiger, A.; Ries, L.; Talbot, R. W.; Dzepina, K.; Deolal, S. P., Atmospheric Peroxyacetyl Nitrate (PAN): A Global Budget and Source Attribution. *Atmos. Chem. Phys.* **2014**, *14*, 2679-2698.
5. Johnson, D.; Marston, G., The Gas-Phase Ozonolysis of Unsaturated Volatile Organic Compounds in the Troposphere. *Chem. Soc. Rev.* **2008**, *37*, 699-716.
6. Khan, M. A. H.; Percival, C. J.; Caravan, R. L.; Taatjes, C. A.; Shallcross, D. E., Criegee Intermediates and their Impacts on the Troposphere. *Environ. Sci. Processes Impacts* **2018**, *20*, 437-453.
7. Chhantyal-Pun, R.; Rotavera, B.; McGillen, M. R.; Khan, M. A. H.; Eskola, A. J.; Caravan, R. L.; Blacker, L.; Tew, D. P.; Osborn, D. L.; Percival, C. J.; Taatjes, C. A.; Shallcross, D. E.; Orr-Ewing, A. J., Criegee Intermediate Reactions with Carboxylic Acids: A Potential Source of Secondary Organic Aerosol in the Atmosphere. *ACS Earth Space Chem.* **2018**, *2*, 833-842.
8. Caravan, R. L.; Vansco, M. F.; Au, K.; Khan, M. A. H.; Li, Y.-L.; Winiberg, F. A. F.; Zuraskia, K.; Lin, Y.-H.; Chao, W.; Trongsiwat, N.; Walsh, P. J.; Osborn, D. L.; Percival, C. J.; Lin, J. J.-M.; Shallcross, D. E.; Sheps, L.; Klippenstein, S. J.; Taatjes, C. A.; Lester, M.

- I., Direct Kinetic Measurements and Theoretical Predictions of an Isoprene-Derived Criegee Intermediate. *Proc. Natl. Acad. USA* **2020**, *117*, 9733-9740.
9. Chao, W.; Hsieh, J.-T.; Chang, C.-H.; Lin, J. J.-M., Direct Kinetic Measurement of the Reaction of the Simplest Criegee Intermediate with Water Vapor. *Science* **2015**, *347*, 751-754.
10. Lewis, T. R.; Blitz, M. A.; Heard, D. E.; Seakins, P. W., Direct Evidence for a Substantive Reaction between the Criegee Intermediate, CH₂OO, and the Water Vapour Dimer. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4859-4863.
11. Taatjes, C. A., Criegee Intermediates: What Direct Production and Detection Can Teach Us About the Reactions of Carboxyl oxides. *Annu. Rev. Phys. Chem.* **2017**, *68*, 183-207.
12. Chhantyal-Pun, R.; Khan, M. A. H.; Taatjes, C. A.; Percival, C. J.; Orr-Ewing, A. J.; Shallcross, D. E., Criegee Intermediates: Production, Detection and Reactivity. *Int. Rev. Phys. Chem.* **2020**, *39*, 383-422.
13. Zhao, Y.; Wingen, L. M.; Perraud, V. r.; Greaves, J.; Finlayson-Pitts, B. J., Role of the Reaction of Stabilized Criegee Intermediates with Peroxy Radicals in Particle Formation and Growth in Air. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12500-12514.
14. Sadezky, A.; Winterhalter, R.; Kanawati, B.; Rompp, A.; Spengler, B.; Mellouki, A.; Bras, G. L.; Chaimbault, P.; Moortgat, G. K., Oligomer Formation during Gas-Phase Ozonolysis of Small Alkenes and Enol Ethers: New Evidence for the Central Role of the Criegee Intermediate as Oligomer Chain Unit. *Atmos. Chem. Phys.* **2008**, *8*, 2667-2699.
15. Sakamoto, Y.; Inomata, S.; Hirokawa, J., Oligomerization Reaction of the Criegee Intermediate Leads to Secondary Organic Aerosol Formation in Ethylene Ozonolysis. *J. Phys. Chem. A* **2013**, *2013*, 12912-12921.
16. Anglada, J. M.; Olivella, S.; Sole, A., The Reaction of Formaldehyde Carbonyl Oxide with the Methyl Peroxy Radical and its Relevance in the Chemistry of the Atmosphere. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18921-18933.
17. Vereecken, L.; Harder, H.; Novelli, A., The Reaction of Criegee Intermediates with NO, RO₂, and SO₂, and Their Fate in the Atmosphere. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14682-14695.
18. Miliordos, E.; Xantheas, S. S., The Origin of the Reactivity of the Criegee Intermediate: Implications for Atmospheric Particle Growth. *Angew. Chem. Int. Ed.* **2015**, *54*, 1-6.
19. Chhantyal-Pun, R.; Khan, M. A. H.; Martin, R.; Zachhuber, N.; Buras, Z. J.; Percival, C. J.; Shallcross, D. E.; Orr-Ewing, A. J., Direct Kinetic and Atmospheric Modeling Studies of Criegee Intermediate Reactions with Acetone. *ACS Earth Space Chem.* **2019**, *3*, 2363-2371.
20. Chhantyal-Pun, R.; Davey, A.; Shallcross, D. E.; Percival, C. J.; Orr-Ewing, A. J., A Kinetic Study of the CH₂OO Criegee Intermediate Self-Reaction, Reaction with SO₂ and Unimolecular Reaction Using Cavity Ring-Down Spectroscopy. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3617-3626.
21. Chhantyal-Pun, R.; McGillen, M. R.; Beames, J. M.; Khan, M. A.; Percival, C. J.; Shallcross, D. E.; Orr-Ewing, A. J., Temperature Dependence of the Rates of Reaction of Trifluoroacetic Acid with Criegee Intermediates. *Angew. Chem. Int. Ed.* **2017**, *56*, 9044-9047.
22. Chhantyal-Pun, R.; Shannon, R. J.; Tew, D. P.; Caravan, R. L.; Duchi, M.; Wong, C.; Ingham, A.; Feldman, C.; McGillen, M. R.; Khan, M. A. H.; Antonov, I. O.; Rotavera, B.; Ramasesha, K.; Osborn, D. L.; Taatjes, C. A.; Percival, C. J.; Shallcross, D. E.; Orr-Ewing, A. J., Experimental and Computational Studies of Criegee Intermediate Reactions with NH₃ and CH₃NH₂. *Phys. Chem. Chem. Phys.* **2019**, *21*, 14042-14052.

23. Welz, O.; Savee, J. D.; Osborn, D. L.; Vasu, S. S.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A., Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2 . *Science* **2012**, 335, 204-207.
24. Ting, W.-L.; Chen, Y.-H.; Chao, W.; Smith, M. C.; Lin, J. J.-M., The UV Absorption Spectrum of the Simplest Criegee Intermediate CH_2OO . *Phys. Chem. Chem. Phys.* **2014**, 16, 10438-10443.
25. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J., Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Volume I – Gas Phase Reactions of Ox, HOx, NOx and SOx Species. *Atmos. Chem. Phys.* **2004**, 4, 1461-1738.
26. Cullen, M. J., The Unified Forecast/Climate Model. *Meteorol. Mag.* **1993**, 122, 81-94.
27. Johns, T. C.; Carnell, R. E.; Crossley, J. F.; Gregory, J. M.; Mitchell, J. F. B.; Senior, C. A.; Tett, S. F. B.; Wood, R. A., The Second Hadley Centre Coupled Ocean-Atmosphere GCM: Model Description, Spinup and Validation. . *Clim. Dyn.* **1997**, 13, 103-134.
28. Granier, C.; Lamarque, J. F.; Mieville, A.; Muller, J. F.; Olivier, J.; Orlando, J.; Peters, J.; Petron, G.; Tyndall, S.; Wallens, S., POET, A Database of Surface Emissions of Ozone Precursors (access date 21 May 2020). 2005.
29. Mikaloff-Fletcher, S. E.; Tans, P. P.; Bruhwiler, L. M.; Miller, J. B.; Heimann, M., CH_4 Sources Estimated from Atmospheric Observations of CH_4 and its $^{13}\text{C}/^{12}\text{C}$ Isotopic Ratios: 1. Inverse Modeling of Source Processes. . *Glob. Biogeochem. Cycles* **2004**, 18, GB4004 1-17.
30. Houweling, S.; Dentener, F.; Lelieveld, J.; Walter, B.; Dlugokencky, E., The Modeling of Tropospheric Methane- How well can Point Measurements be Reproduced by a Global Model? . *J. Geophys. Res.* **2000**, 105, 8981-9002.
31. Olivier, J. G.; Bouwman, A. F.; Berdowski, J. J.; Veldt, C.; Bloos, J. P.; Visschedijk, A. J.; Zandveld, P. Y.; Haverlag, J. L. *A Set of Global Emission Inventories of Greenhouse Gases and Ozone-Depleting Substances for all Anthropogenic and most Natural Sources on a Per Country Basis and on 1 degree x 1 Degree Grid. Technical Report (RIVM report nr 771060002)*; National Institute for Public Health and the Environment, Netherlands, 1996.
32. Cox, P. M. *Description of the TRIFFID Dynamic Global Vegetation Model, Hadley Centre Technical Note No. 24*; Met Office, Exeter, UK, 2001.
33. Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P., A Global Model of Natural Volatile Organic Compound Emissions *J. Geophys. Res.* **1995**, 100, 8873-8892.
34. Guenther, A. B.; Jiang, X.; Heald, C. L.; Sakulyanontvittaya, T.; Duhl, T.; Emmons, L. K.; Wang, X., The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): An Extended and Updated Framework for Modeling Biogenic Emissions. *Geosci. Model Dev.* **2012**, 5, 1471-1492.
35. Jenkin, M. E.; Watson, L. A.; Utembe, S. R.; Shallcross, D. E., A Common Representative Intermediates (CRI) Mechanism for VOC degradation. Part 1: Gas Phase Mechanism Development. *Atmos. Environ.* **2008**, 42, 7185-7195.
36. Watson, L. A.; Shallcross, D. E.; Utembe, S. R.; Jenkin, M. E., A Common Representative Intermediates (CRI) Mechanism for VOC Degradation. Part 2: Gas Phase Mechanism Reduction. *Atmos. Environ.* **2008**, 42, 7196-7204.

37. Utembe, S. R.; Watson, L. A.; Shallcross, D. E.; Jenkin, M. E., A Common Representative Intermediates (CRI) Mechanism for VOC Degradation. *Atmos. Environ.* **2009**, *43*, 1982-1990.
38. Utembe, S. R.; Cooke, M. C.; Archibald, A. T.; Shallcross, D. E.; Derwent, R. G.; Jenkin, M. E., Simulating Secondary Organic Aerosol in a 3-D Lagrangian Chemistry Transport Model using the Reduced Common Representative Intermediates Mechanism (CRI v2-R5). *Atmos. Environ.* **2011**, *45*, 1604-1614.
39. Khan, M. A. H.; Jenkin, M. E.; Foulds, A.; Derwent, R. G.; Percival, C. J.; Shallcross, D. E., A Modeling Study of Secondary Organic Aerosol Formation From Sesquiterpenes using the STOCHEM Global Chemistry and Transport Model. *J. Geophys. Res. Atmos.* **2017**, *122*, 4426-4439.
40. Jenkin, M. E.; Khan, M. A. H.; Shallcross, D. E.; Bergström, R.; Simpson, D.; Murphy, K. L. C.; Rickard, A. R., The CRI v2.2 Reduced Degradation Scheme for Isoprene. *Atmos. Environ.* **2019**, *212*, 172-182.
41. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J., Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Volume II – Gas Phase Reactions of Organic Species. *Atmos. Chem. Phys.* **2006**, *6*, 3625-4035.
42. Khamaganov, V.; Karunanandan, R.; Rodriguez, A.; Crowley, J. N., Photolysis of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (248 nm, 266 nm), $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ (248 nm) and $\text{CH}_3\text{C}(\text{O})\text{Br}$ (248 nm): Pressure Dependent Quantum Yields of CH_3 Formation. *Phys. Chem. Chem. Phys.* **2007**, *2007*, 4098-4113.
43. Khamaganov, V. G.; Karunanandan, R.; Horowitz, A.; Dillon, T. J.; Crowley, J. N., Photolysis of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ at 248 and 266 nm: Pressure and Temperature Dependent Overall Quantum Yields. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6173-6181.
44. Carr, S. A.; Glowacki, D. R.; Liang, C.-H.; Baeza-Romero, M. T.; Blitz, M. A.; Pilling, M. J.; Seakins, P. W., Experimental and Modeling Studies of the Pressure and Temperature Dependences of the Kinetics and the OH Yields in the Acetyl + O_2 Reaction. *J. Phys. Chem. A* **2011**, *115*, 1069-1085.
45. Dillon, T. J.; Tucceri, M. a. E.; Crowley, J. N., Laser Induced Fluorescence Studies of Iodine Oxide Chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5185-5198.
46. McGillen, M. R.; Curchod, B. F. E.; Chhantyal-Pun, R.; Beames, J. M.; Watson, N.; Khan, M. A. H.; McMahon, L.; Shallcross, D. E.; Orr-Ewing, A. J., Criegee Intermediate-Alcohol Reactions, A Potential Source of Functionalized Hydroperoxides in the Atmosphere. *ACS Earth Space Chem.* **2017**, *1*, 664-672.
47. Welz, O.; Eskola, A. J.; Sheps, L.; Rotavera, B.; Savee, J. D.; Scheer, A. M.; Osborn, D. L.; Lowe, D.; Booth, A. M.; Xiao, P.; Khan, M. A. H.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A., Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic and Acetic Acid Near the Collision Limit: Direct Kinetics Measurements and Atmospheric Implications. *Angew. Chem. Int. Ed.* **2014**, *53*, 4547-4550.
48. Berndt, T.; Herrmann, H.; Kurtén, T., Direct Probing of Criegee Intermediates from Gas-Phase Ozonolysis using Chemical Ionization Mass Spectrometry. *J. Am. Chem. Soc.* **2017**, *139*, 13387-13392.
49. Sindelarova, K.; Granier, C.; Bouarar, I.; Guenther, A.; Tilmes, S.; Stavrakou, T.; Müller, J.-F.; Kuhn, U.; Stefani, P.; Knorr, W., Global Data Set of Biogenic VOC Emissions

Calculated by the MEGAN Model over the Last 30 Years. *Atmos. Chem. Phys.* **2014**, *14*, 9317-9341.

50. Nguyen, T. L.; Peeters, J.; Vereecken, L., Theoretical Study of the Gas-Phase Ozonolysis of β -Pinene ($C_{10}H_{16}$). *Phys. Chem. Chem. Phys.* **2009**, *11*, 5643-5656.
51. Ahrens, J.; Carlsson, P. T. M.; Hertl, N.; Olzmann, M.; Pfeifle, M.; Wolf, J. L.; Zeuch, T., Infrared Detection of Criegee Intermediates Formed During the Ozonolysis of β -Pinene and their Reactivity Towards Sulfur Dioxide. *Angew. Chem. Int. Ed.* **2014**, *53*, 715-719.
52. Winterhalter, R.; Neeb, P.; Grossmann, D.; Kolloff, A.; Horie, O.; Moortgat, G., Products and Mechanism of the Gas Phase Reaction of Ozone with β -Pinene. *J. Atmos. Chem.* **2000**, *35*, 165-197.
53. IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. <http://iupac.pole-ether.fr> (accessed 12 May, 2020).
54. Newland, M. J.; Rickard, A. R.; Sherwen, T.; Evans, M. J.; Vereecken, L.; Muñoz, A.; Ródenas, M.; Bloss, W. J., The Atmospheric Impacts of Monoterpene Ozonolysis on Global Stabilised Criegee Intermediate Budgets and SO_2 Oxidation: Experiment, Theory and Modelling. *Atmos. Chem. Phys.* **2018**, *18*, 6095-6120.
55. Sipilä, M.; Jokinen, T.; Berndt, T.; Richters, S.; Makkonen, R.; Donahue, N. M.; III, R. L. M.; Kurtén, T.; Paasonen, P.; Sarnela, N.; Ehn, M.; Junninen, H.; Rissanen, M. P.; Thornton, J.; Stratmann, F.; Herrmann, H.; Worsnop, D. R.; Kulmala, M.; Kerminen, V.-M.; T. Petäjä, Reactivity of Stabilized Criegee Intermediates (sCIs) from Isoprene and Monoterpene Ozonolysis Toward SO_2 and Organic Acids. *Atmos. Chem. Phys.* **2014**, *14*, 12143-12153.
56. The Master Chemical Mechanism. <http://mcm.leeds.ac.uk/MCM> (accessed May 14, 2020).
57. Reissell, A.; Aschmann, S. M.; Atkinson, R.; Arey, J., Products of the OH Radical- and O_3 -Initiated Reactions of Myrcene and Ocimene. *J. Geophys. Res.* **2002**, *107*, ACH 3-1-ACH 3-6.
58. Fang, Y.; Barber, V. P.; Klippenstein, S. J.; McCoy, A. B.; Lester, M. I., Tunneling Effects in the Unimolecular Decay of $(CH_3)_2COO$ Criegee Intermediates to OH Radical Products. *J. Chem. Phys.* **2017**, *146*, 134307 1-9.
59. Fang, Y.; Liu, F.; Barber, V. P.; Klippenstein, S. J.; McCoy, A. B.; Lester, M. I., Communication: Real Time Observation of Unimolecular Decay of Criegee Intermediates to OH Radical Products. *J. Chem. Phys.* **2016**, *144*, 061102 1-4.
60. Vereecken, L.; Novelli, A.; Taraborrelli, D., Unimolecular Decay Strongly Limits the Atmospheric Impact of Criegee Intermediates. *Phys. Chem. Chem. Phys.* **2017**, *19*, 31599-31612.
61. Drozd, G. T.; Donahue, N. M., Pressure Dependence of Stabilized Criegee Intermediate Formation from a Sequence of Alkenes. *J. Phys. Chem. A* **2011**, *115*, 4381-4387.
62. Lin, L.-C.; Chao, W.; Chang, C.-H.; Takahashi, K.; Lin, J. J.-M., Temperature Dependence of the Reaction of Anti- CH_3CHOO with Water Vapor. *Phys. Chem. Chem. Phys.* **2016**, *18*, 28189-28197.
63. Fang, Y.; Liu, F.; Klippenstein, S. J.; Lester, M. I., Direct Observation of Unimolecular Decay of CH_3CH_2CHOO Criegee Intermediates to OH Radical Products. *J. Chem. Phys.* **2016**, *145*, 044312-1-8.
64. Novelli, A.; Hens, K.; Ernest, C. T.; Martinez, M.; Nölscher, A. C.; Sinha, V.; Paasonen, P.; Petäjä, T.; Sipilä, M.; Elste, T.; Plass-Dülmer, C.; Phillips, G. J.; Kubistin, D.; Williams, J.; Vereecken, L.; Lelieveld, J.; Harder, H., Estimating the Atmospheric

Concentration of Criegee Intermediates and Their Possible Interference in a FAGE-LIF Instrument. *Atmos. Chem. Phys.* **2017**, *17*, 7807-7826.

65. Jenkin, M. E., Modelling the Formation and Composition of Secondary Organic Aerosol from α - and β -Pinene Ozonolysis using MCM v3. *Atmos. Chem. Phys.* **2004**, *4*, 1741-1757.
66. Multiphase System Online Property Prediction.
http://umansysprop.seaes.manchester.ac.uk/tool/vapour_pressure (accessed 2 January 2020).
67. Nannoolal, Y.; Rarey, J.; Ramjugernatha, D., Estimation of Pure Component Properties Part 3. Estimation of the Vapor Pressure of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions. *Fluid Phase Equilibria* **2008**, *269*, 117-133.
68. Nannoolal, Y.; Rarey, J.; Ramjugernatha, D.; Cordesb, W., Estimation of Pure Component Properties Part 1. Estimation of the Normal Boiling Point of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions. *Fluid Phase Equilibria* **2004**, *226*, 45-63.
69. O'Meara, S.; Booth, A. M.; Barley, M. H.; Topping, D.; McFiggans, G., An Assessment of Vapour Pressure Estimation Methods. *Phys. Chem. Chem. Phys.* **2014**, *16*, 19453-19469.
70. Vereecken, L.; Nguyen, H. M. T., Theoretical Study of the Reaction of Carbonyl Oxide with Nitrogen Dioxide: $\text{CH}_2\text{OO} + \text{NO}_2$. *Int. J. Chem. Kinet.* **2017**, *49*, 752-760.
71. Luo, P.-L.; Chung, C.-A.; Lee, Y.-P., Rate Coefficient of the Reaction $\text{CH}_2\text{OO} + \text{NO}_2$ Probed with a Quantum-Cascade Laser near 11 μm . *Phys. Chem. Chem. Phys.* **2019**, *21*, 17578-17583.
72. Taatjes, C. A.; Welz, O.; Eskola, A. J.; Savee, J. D.; Scheer, A. M.; Shallcross, D. E.; Rotavera, B.; Lee, E. P. F.; Dyke, J. M.; Mok, D. K. W.; Osborn, D. L.; Percival, C. J., Direct Measurements of Conformer-Dependent Reactivity of the Criegee Intermediate CH_3CHOO . *Science* **2013**, *340*, 177-180.
73. Chhantyal-Pun, R.; Welz, O.; Savee, J. D.; Eskola, A. J.; Lee, E. P. F.; Blacker, L.; Hill, H. R.; Ashcroft, M.; Khan, M. A. H.; Lloyd-Jones, G. C.; Evans, L.; Rotavera, B.; Huang, H.; Osborn, D. L.; Mok, D. K. W.; Dyke, J. M.; Shallcross, D. E.; Percival, C. J.; Orr-Ewing, A. J.; Taatjes, C. A., Direct Measurements of Unimolecular and Bimolecular Reaction Kinetics of the Criegee Intermediate $(\text{CH}_3)_2\text{COO}$. *J. Phys. Chem. A* **2017**, *121*, 4-15.
74. Nguyen, T. B.; Tyndall, G. S.; Crounse, J. D.; Teng, A. P.; Bates, K. H.; Schwantes, R. H.; Coggon, M. M.; Zhang, L.; Feiner, P.; Miller, D. O.; Skog, K. M.; Rivera-Rios, J. C.; Dorris, M.; Olson, K. F.; Koss, A.; Wild, R. J.; Brown, S. S.; Goldstein, A. H.; Gouw, J. A. d.; Brune, W. H.; Keutsch, F. N.; Seinfeld, J. H.; Wennberg, P. O., Atmospheric Fates of Criegee Intermediates in the Ozonolysis of Isoprene. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10241-10254.
75. Barber, V. P.; Pandit, S.; Green, A. M.; Trongsiwat, N.; Walsh, P. J.; Klippenstein, S. J.; Lester, M. I., Four Carbon Criegee Intermediate from Isoprene Ozonolysis: Methyl Vinyl Ketone Oxide Synthesis, Infrared Spectrum, and OH Production. *J. Am. Chem. Soc.* **2018**, *140*, 10866-10880.
76. Wennberg, P. O.; Bates, K. H.; Crounse, J. D.; Dodson, L. G.; McVay, R. C.; Mertens, L. A.; Nguyen, T. B.; Praske, E.; Schwantes, R. H.; Smarte, M. D.; Clair, J. M. S.; Teng, A. P.; Zhang, X.; Seinfeld, J. H., Gas-Phase Reactions of Isoprene and Its Major Oxidation Products. *Chem. Rev.* **2018**, *118*, 3337-3390.

For TOC only