Kinetics of stabilised Criegee intermediates derived from alkene ozonolysis: reactions with SO2, H2O and decomposition under boundary layer conditions

Mike J. Newland, Andrew R. Rickard, Mohammed S. Alam, Luc Vereecken, Amalia Muñoz, Milagros Ródenas and William J. Bloss

The removal of SO2 in the presence of alkene–ozone systems has been studied for ethene, cis-but-2-ene, trans-but-2-ene and 2,3-dimethyl-but-2-ene, as a function of humidity, under atmospheric boundary layer conditions. The SO2 removal displays a clear dependence on relative humidity for all four alkene–ozone systems confirming a significant reaction for stabilised Criegee intermediates (SCI) with H2O. The observed SO2 removal kinetics are consistent with relative rate constants, k(SCI + H2O)/k(SCI + SO2), of 3.3 (±1.1) x 10^-5 for CH2OO, 26 (±10) x 10^-5 for CH3CHOO derived from cis-but-2-ene, 33 (±10) x 10^-5 for CH3CHOO derived from trans-but-2-ene, and 8.7 (±2.5) x 10^-5 for (CH3)2COO derived from 2,3-dimethyl-but-2-ene. The relative rate constants for k(SCI decomposition)/k(SCI + SO2) are -2.3 (±3.5) x 10^11 cm^-3 for CH2OO, 13 (±43) x 10^11 cm^-3 for CH3CHOO derived from cis-but-2-ene, -14 (±31) x 10^11 cm^-3 for CH3CHOO derived from trans-but-2-ene and 63 (±14) x 10^13 cm^-3 for (CH3)2COO. Uncertainties are ±2r and represent combined systematic and precision components. These values are derived following the approximation that a single SCI is present for each system; a more comprehensive interpretation, explicitly considering the differing reactivity for syn- and anti-SCI formers, is also presented. This yields values of 3.5 (±3.1) x 10^-4 for k(SCI + H2O)/k(SCI + SO2) of anti-CH3CHOO and 1.2 (±1.1) x 10^13 for k(SCI decomposition)/k(SCI + SO2) of syn-CH3CHOO. The reaction of the water dimer with CH2OO is also considered, with a derived value for k(CH2OO + (H2O)2)/k(CH2OO + SO2) of 1.4 (±1.8) x 10^-2. The observed SO2 removal rate constants, which technically represent upper limits, are consistent with decomposition being a significant, structure dependent, sink in the atmosphere for syn-SCI.

1. Introduction

Atmospheric oxidation processes are central to understanding trace gas atmospheric composition, the abundance of air pollutants harmful to human health, crops and ecosystems, and the removal of reactive greenhouse gases such as methane. The principal atmospheric oxidants responsible for initiating the gas-phase degradation of volatile organic compounds (VOCs), NOx, and SO2 are OH, NOx and O3, with additional contributions from other species such as halogen atoms. Recent field measurements in a boreal forest have identified the presence of an additional oxidant species, removing SO2 and producing H2SO4. The additional SO2 oxidation observed was substantial (comparable to that due to OH radicals alone), and attributed to a product of alkene ozonolysis – the boreal forest environment being one in which substantial biogenic alkene emissions occur – suggested to be the stabilised Criegee intermediate (SCI). The gas-phase oxidation of SO2 in the atmosphere is of interest to climate research as it leads to formation of H2SO4, contributing to new particle formation and sulphate aerosol loading, in competition with condensed phase oxidation. A missing mechanism for the conversion of SO2 to H2SO4 could lead to model underestimation of the sulphate aerosol burden and affect radiative forcing calculations, with corresponding implications for climate predictions. Enhanced SO2 oxidation in alkene–ozone systems was first reported by Cox & Penkett over forty years ago, however the precise reaction mechanism giving rise to this effect remains elusive. The “Criegee” ozonolysis reaction mechanism was first postulated in the 1940s. It is now accepted that the ozone
molecule adds to the C=O double bond via a concerted cycloaddition to form a primary ozonide, followed by cleavage of the C-C bond and one of the O-O bonds forming a carbonyl molecule and a carbonyl oxide, or 'Criegee intermediate' (CI). Ozonolysis derived SCIs are formed with a broad internal energy distribution, to yield chemically activated and stabilised SCIs. SCIs can have sufficiently long lifetimes to undergo bimolecular reactions with H2O and SO2 amongst other species. Chemically activated SCIs may also undergo collisional stabilisation, unimolecular decomposition or isomerisation (Scheme 1). For substituted alkenes, SCIs can undergo a 1,4-H-shift rearrangement through a vinyl-hydroperoxide (VHP) via the so-called “hydroperoxide channel” and decompose to yield OH and a vinyloxyl radical – a substantial non-photolytic source of atmospheric oxidants. This is the favoured channel for SCIs formed in the syn-configuration. Time resolved studies show that the VHP may persist for appreciable timescales under boundary layer conditions, giving rise to the observed pressure dependence of OH radical yields, and opening the possibility for bimolecular reactions of this species to occur. SCIs formed in the anti-configuration are thought to primarily undergo rearrangement and decomposition via a dioxirane intermediate (“the acid/ester channel”), producing a range of daughter products and contributing to the observed overall HO2 radical yield.

$$\text{Alkene} + \text{O}_3 \xrightarrow{k_1} \phi\text{SCI} + (1-\phi)\text{CI} + \text{RCHO} \quad (R1)$$

$$\text{SCI} + \text{SO}_2 \xrightarrow{k_2} \text{SO}_3 + \text{RCHO} \quad (R2)$$

$$\text{SCI} + \text{H}_2\text{O} \xrightarrow{k_3} \text{products} \quad (R3)$$

$$\text{SCI} \xrightarrow{k_4} \text{products} \quad (R4)$$

Until recently, it has been thought that the predominant atmospheric fate for SCIs was reaction with water vapour – leading to a significant source of organic acids and hydroperoxides, suggesting that bimolecular reaction with SCIs is an unimportant oxidation mechanism for trace gas species. This view was recently challenged by direct observation and kinetic studies of the CH3OO and CH3CHOO SCIs.

Taatjes and co-workers directly observing CI kinetics for the first time, found reactions of CH3OO with SO2 and NO2 to be substantially faster than previously thought, pointing to a potentially important role for this species in atmospheric SO2 and NO2 oxidation; subsequent measurements have identified SO3 (ref. 16) and NO3 (ref. 18) as products of these reactions. The key to whether SCIs are indeed significant contributors to gas-phase atmospheric SO2 oxidation is the ratio of the rate constants for reaction of the SCI with SO2 ($k_d$) to that with H2O ($k_d$) and decomposition ($k_d$). In laboratory studies where SCIs were produced by the 248 nm laser photolysis of alkyl iodide precursors at 4 Torr total pressure, with the SCI decay monitored by VUV photoionisation in the presence of excess co-reactants, this ratio has recently been reported to be $10^3$–$10^4$ for the smallest two SCIs (CH2OO,15,17 and CH3CHOO16), with $k_d$ on the order of $10^{-11}$ cm$^3$ s$^{-1}$ and $k_d$ on the order of $10^{-15}$ cm$^3$ s$^{-1}$. In contrast, alternative studies of SO2 oxidation in alkene–ozone systems, performed at atmospheric pressure through detection of the H2SO4 product, find much smaller SCI + SO2 rate coefficients (by ca. two orders of magnitude).19

An additional, potentially important, fate of SCI under atmospheric conditions is unimolecular decomposition (denoted $k_d$ in (R4)). For CH2OO, rearrangement via a ‘hot’ acid species represents the lowest accessible decomposition channel, but due to lack of alkyl substituents, the theoretically predicted 298 K rate constant is rather low, 0.3 s$^{-1}$,22 Previous studies have identified the hydroperoxide rearrangement as dominant for SCIs with a syn configuration, determining their overall unimolecular decomposition rate.19

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is somewhat smaller than but comparable in magnitude to an earlier measurement of 6.4 s⁻¹ (determined at 100 Torr). Theoretical estimates of (CH₃)₂C·OO decomposition rates are higher, at up to 250 s⁻¹. Photolysis loss rates have also recently been reported for CH₂OO₂ and CH₃CHOO. In the presence of varying amounts of water in the European Photochemical Reactor facility (EUPHORE), Valencia, Spain.

2. Experimental

2.1 EUPHORE

EUPHORE is a 200 m³ simulation chamber used for studying reaction mechanisms under atmospheric boundary layer conditions. In general, experiments comprised time-resolved measurement of the removal of SO₂ in the presence of an alkene-ozone system, as a function of humidity. SO₂ and O₃ abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. The precision of the SO₂ and O₃ monitors was 0.25 and 0.47 ppbv respectively (evaluated as 2 standard deviations of the measured value prior to SO₂ or O₃ addition). The chamber is fitted with large horizontal and vertical fans to ensure rapid mixing (three minutes). Further details of the chamber setup and instrumentation are available elsewhere.

2.2 Experimental approach

Experimental procedure, starting with the chamber filled with clean air, comprised addition of SF₆ and cyclohexane, followed by water vapour, O₃ (ca. 500 ppbv) and SO₂ (ca. 50 ppbv). A gap of five minutes was left prior to addition of the alkene, to allow complete mixing. The reaction was then initiated by addition of the alkene (ca. 500 ppbv for ethene, 200 ppbv for cis- and trans-but-2-ene and 400 ppbv for TME). The chamber was monitored for an hour subsequent to the addition of ethene and forty five minutes for cis- and trans-but-2-ene and TME. The rate of alkene-ozone consumption is dependent on kₙ. Roughly 25% of the ethene was consumed after an hour, while for cis- and trans-but-2-ene and TME 90% of the alkene was consumed within roughly 25 minutes, 20 minutes and 6 minutes respectively. Each experiment was performed at a constant humidity, which was increased in a step-wise manner for consecutive runs to cover the range 1.5–21% RH. Measured increases in [SO₂] agreed with measured volumetric addition across the SO₂ and humidity range used in the experiments.

2.3 Analysis approach

The following sections describe (i) a common analysis applied to all systems, but which features several approximations, and (ii) more detailed consideration of each chemical system in turn, to address potential contributions from the water dimer, and multiple criegee species within each system (e.g. contrasting reactivity of different SCI conformers).

From the chemistry presented in reactions (R1)–(R4) it is assumed that SCI will be produced in the chamber from the reaction of the alkene with ozone at a given yield, φ. The SCI produced can then react with SO₂, with H₂O, with other species or decompose under the experimental conditions applied. The rate at which SO₂ is lost, compared with the total production of SCI, is determined by the fraction, f, of the total SCI produced which reacts with SO₂, compared to the sum of the total loss processes of the SCI (eqn (E1)):

\[
f = \frac{k_2[SO_2]}{k_2[SO_2] + k_3[H_2O] + k_d + L}
\]

\[
\frac{dSO_2}{dO_3} = \phi \cdot f
\]

Here, L is the sum of any other pseudo-first order chemical loss processes for SCI in the chamber, after correction for dilution. (E2) neglects other (non-alkene) chemical sinks for O₃, such as reaction with HO₂ – also produced directly during alkene ozonolysis, but indicated through model calculations to account for <2% of ozone loss under all the experimental conditions of this work. Eqn (E1) and (E2) treat the SCIs formed as a single species – this is the case for (e.g.) ethene and TME, but is an approximation for the 2-butenes; considered further below.

2.3.1 SCI yield calculation. Values for φ_{SCI} were determined for each ozonolysis reaction from experiments performed under dry conditions (RH < 1%) in the presence of excess SO₂ (ca. 1000 ppbv), such that SO₂ scavenges the overwhelming majority of the SCI. From eqn (E2), regressing dSO₂ against dO₃ (corrected for chamber dilution), assuming f to be unity (i.e. all the SCI produced reacts with SO₂) determines the value of φ_{min}, a lower limit to the SCI yield. Fig. 2 shows the experimental data, from which φ_{min} was derived, for all four alkene ozonolysis systems studied.

The lower limit criterion applies as in reality f will be less than one, at experimentally accessible SO₂ levels, as a small fraction of the SCI will still react with any H₂O present, or undergo decomposition. The actual yield, φ, was determined by combining the results from the high-SO₂ experiments with those from the series of experiments performed at lower SO₂, as a function of [H₂O], to determine kₙ/k₂ and kₙ/k₃ (see Section 2.3.2), through an iterative process to determine the single unique value of φ_{SCI} which fits both datasets. It is important to note that the SCI yield is to an extent an operationally defined quantity – for example, OH formation from alkene ozonolysis is known to proceed over...
at least hundreds of milliseconds following the alkene–ozone reaction, and so the corresponding CI population must also be evolving with time. In this work, SCI yields reflect the amount of SCI available to oxidise SO₂ on timescales of seconds to minutes.

2.3.2 $k_{\text{SCI} + \text{H}_2\text{O}}/k_{\text{SCI} + \text{SO}_2}$ and $k_3/k_{\text{SCI} + \text{SO}_2}$. To determine $k_3/k_2$ and $k_2/k_{\text{SCI} + \text{SO}_2}$, a series of experiments were performed for each alkene, in which the SO₂ loss was monitored as a function of $[\text{H}_2\text{O}]$. From eqn (E2), regression of the loss of ozone (dO₃) against the loss of SO₂ (dSO₂) (both corrected for dilution, measured through the removal of SF₆, added at the start of each experiment and monitored via FTIR) for an experiment determines the factor $f_\phi$ at a given point in time. This quantity will vary through the experiment as SO₂ is consumed, and other potential SCI co-reactants are produced, as predicted by eqn (E1). A smoothed fit was applied to the experimental data for the cumulative consumption of SO₂ and O₃, ∆SO₂ and ∆O₃, (Fig. 1) to determine dSO₂/dO₃ (and hence each experiment, for use in eqn (E3). The start of the experiment (i.e. when $[\text{SO}_2] \sim 50$ ppbv) was used as this corresponds to the greatest rate of production of the SCI, and hence the largest experimental signals (O₃ and SO₂ rate of change) and is the point at which the SCI + SO₂ reaction has the greatest magnitude compared with any other potential chemical loss processes for either species (see discussion below).

$$[\text{SO}_2](1/f - 1) = \frac{k_3}{k_2}[\text{H}_2\text{O}] + \frac{k_4 + L}{k_2}$$ (E3)

The value $[\text{SO}_2]/(1/f - 1)$ can then be regressed against $[\text{H}_2\text{O}]$ for each experiment to give a plot with a gradient of $k_3/k_2$ and an intercept of $(k_4 + L)/k_2$ (eqn (E3)). Our data cannot determine absolute rate constants (i.e. values of $k_3$, $k_4$, $k_2$) in isolation, but is limited to assessing their relative values, which may be placed on an absolute basis through use of an (external) reference value. Eqs (E1)–(E3) as presented above assume that only a single SCI species is present in each ozonolysis system. While this is the case for the ethene and TME systems, for the but-2-ene systems this is an approximation as two conformers of the CH₃CHOO SCI (syn and anti) are produced. Further analysis is performed in Section 3.3.2 in which the SO₂ loss in the but-2-ene systems is treated as having two components, related to the different SCI.

3. Results and discussion

3.1 Introduction

Table 1 shows the resulting SCI yields obtained for the ozonolysis of ethene, cis-but-2-ene, trans-but-2-ene and tetramethylethylene (TME); uncertainties are ±2σ, and represent the combined systematic (estimated measurement uncertainty) and precision components. Also shown are past literature values, obtained under various conditions using a range of different SCI scavengers.

The yield of CH₃OO from ethene ozonolysis obtained in this work is 0.37 (±0.04). This yield has been investigated in many previous studies, with values ranging from 0.34–0.50 determined – a more detailed review is available elsewhere. The yield obtained in this work is at the lower end of but within the envelope of these estimates, and is in excellent agreement with the current IUPAC recommendation of 0.37.

The yield of CH₃CHOO from cis-but-2-ene ozonolysis obtained in this work is 0.38 (±0.05), with that from trans-but-2-ene being 0.28 (±0.03). These values fall within the range of reported literature values of 0.18–0.43 and 0.13–0.53 for cis-but-2-ene and trans-but-2-ene respectively (Table 1). cis and trans-but-2-ene both yield (differing) mixtures of syn and anti conformers of CH₃CHOO, the relative amounts of which are not well known, and which are treated here initially as a single SCI species (this approximation is discussed further in Section 3.3), Berndt et al. recently reported a yield of 0.49 (±0.22) for the CH₃CHOO produced from trans-but-2-ene ozonolysis (also treating both syn and anti conformers as a single SCI species).

The yield of (CH₃)₂COO from TME ozonolysis obtained in this work is 0.32 (±0.02). This again falls within the (wide) range in the literature of 0.10–0.65, with Berndt et al. most recently reporting a yield of 0.45 (±0.20).
Table 1. SCI yields derived in this work and reported in the literature. Uncertainty ranges (±2σ, parentheses) indicate combined precision and systematic measurement error components for this work, and are given as stated for literature studies. All referenced studies were conducted between 700 and 760 Torr. C2B – derived from cis-but-2-ene; T2B – derived from trans-but-2-ene.

<table>
<thead>
<tr>
<th>SCI</th>
<th>φSCI</th>
<th>Ref.</th>
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<tr>
<td>CHOO</td>
<td>0.37 (±0.04)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>MCMv3.2a (IUPAC)33</td>
</tr>
<tr>
<td></td>
<td>0.35 (±0.05)</td>
<td>Niki et al.34</td>
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<tr>
<td></td>
<td>0.39 (±0.053)</td>
<td>Hatakeyama et al.35</td>
</tr>
<tr>
<td></td>
<td>0.47 (±0.05)</td>
<td>Horie and Moortgat36</td>
</tr>
<tr>
<td></td>
<td>0.50 (±0.04)</td>
<td>Neeb et al.27</td>
</tr>
<tr>
<td></td>
<td>0.39 (±0.11)</td>
<td>Hasson et al.38</td>
</tr>
<tr>
<td></td>
<td>0.54 (±0.15)</td>
<td>Alam et al.19</td>
</tr>
<tr>
<td>C2B, CHOO</td>
<td>0.38 (±0.05)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>Rickard et al.19</td>
</tr>
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<td>0.18</td>
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<td></td>
<td>0.43</td>
<td>Cox and Penkett41</td>
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<tr>
<td>T2B, CHOO</td>
<td>0.28 (±0.03)</td>
<td>This work</td>
</tr>
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<td></td>
<td>0.49 (±0.22)</td>
<td>Berndt et al.32</td>
</tr>
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<td></td>
<td>0.53 (±0.24)</td>
<td>Berndt et al.19</td>
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<tr>
<td></td>
<td>0.45</td>
<td>Cox and Penkett41</td>
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<td></td>
<td>0.19 (±0.03)</td>
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<tr>
<td>(CH3)2COO</td>
<td>0.32 (±0.02)</td>
<td>This work</td>
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<td></td>
<td>0.45 (±0.20)</td>
<td>Berndt et al.32</td>
</tr>
<tr>
<td></td>
<td>0.62 (±0.28)</td>
<td>Berndt et al.19</td>
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<td></td>
<td>ca. 0.633</td>
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<td></td>
<td>0.20 (±0.03)</td>
<td>Hasson et al.38</td>
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<td></td>
<td>0.30</td>
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<tr>
<td></td>
<td>0.11</td>
<td>Rickard et al.19</td>
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Table 2. SCI relative rate constants derived in this work using the single-SCI water monomer approach (i.e. eqn (E3); see text). Uncertainty ranges (±2σ, parentheses) indicate combined precision and systematic measurement error components.

<table>
<thead>
<tr>
<th>SCI</th>
<th>10^5 k_d/k_s</th>
<th>10^-13 cm^-3 k_d/k_s</th>
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<tbody>
<tr>
<td>CH2OO</td>
<td>3.3 (±1.1)</td>
<td>-2.3 (±3.5)</td>
</tr>
<tr>
<td>CH3CHOO (C2B)</td>
<td>26 (±10)</td>
<td>13 (±43)</td>
</tr>
<tr>
<td>CH3CHOO (T2B)</td>
<td>33 (±10)</td>
<td>-14 (±31)</td>
</tr>
<tr>
<td>(CH3)2COO</td>
<td>8.7 (±2.5)</td>
<td>63 (±14)</td>
</tr>
</tbody>
</table>

Fig. 1 shows the cumulative consumption of SO2 relative to that of O3, ΔSO2 versus ΔO3 (after correction for dilution), as a function of [H2O] for each experiment for the four alkenes studied. A fit to each experiment, extrapolating the experimental data to estimate SO2 addition at t = 0 (start of each experimental run) for use in eqn (E1)–(E3), is also shown. The overall change in SO2, ΔSO2, is seen to decrease substantially with increasing humidity (over a relatively narrow range of RH (1.5–20%)) for all four alkenes. This trend would be expected from the understood chemistry (R1)–(R3)), as there is competition between SO2, H2O, and decomposition for reaction with the SCI.

Fig. 3 shows a fit of eqn (E3) to the data for each alkene, giving a slope of k_d/k_s and an intercept of (k_s + L)/k_s. The results appear to show a generally linear relationship; however, for cis- and trans-but-2-ene and TME, the data point at the highest relative humidity accessible in this work ([H2O] = 1.5–2.0 × 10^17 cm^-3) appears to deviate from this relationship. These data points lie outside the 95% confidence intervals defined by all the other (lower relative humidity) data for each alkene. For the analysis to determine k_d/k_s and (k_s + L)/k_s presented in Table 2, the points at the highest RH are excluded and the kinetic parameters are derived from a linear fit to the measurements from all other experiments. Extended analyses to account for the non-linearity observed for CH3CHOO and (CH3)2COO are presented in the following sections.

One potential explanation for the observed curvature in the CH3CHOO and (CH3)2COO data is measurement error. ΔSO2 is relatively small at high [H2O] compared to the precision of the measurements; however, even allowing for associated uncertainties, the points at high RH do not fit the linear relationship successfully applied to the remaining data points. Moreover, any systematic error in the measurement of O3, SO2 or H2O would also be expected to affect the results for the ethene system (and to a greater extent, given the slow ethene-ozone reaction rate and consequent lower overall chemical SO2 loss observed), suggesting that the cause lies in contrasting chemical behaviour. In terms of experimental factors, H2O was measured using multiple approaches (two dew-point hygrometers in addition to a solid state probe) with no evidence for any divergence with RH. SO2 monitors can exhibit humidity-dependent interferences (quenching of the SO2 signal), commonly of the order of a few percent, observed at very high RH, and corrected through incorporation of a nafion dryer (fitted in this case); in addition the monitor-derived SO2 concentration increments were in agreement with those calculated from the measured SO2 addition and chamber volume, across the relative humidity range studied.

It should be noted that the k_d values reported here represent upper limits, as a consequence of possible further chemical losses for the SCI within our experimental system (as represented by L in eqn (E3), notwithstanding the approach of extrapolating to the start of each experiment to minimise these). Other potential
fates for SCIs include reaction with ozone,42,43 other SCI,43 carbonyl products,44 acids,45 or with the parent alkene45 itself. Sensitivity analyses indicate that the reaction with ozone could be significant, as predicted by theory42,43 with a possible contribution of up to 10% of SCI loss for \((\text{CH}_3)\text{OO}\) at 2% RH, while total losses from reaction with SCI (self-reaction), carbonyls and alkenes are calculated to account for <1% of the total SCI loss under the experimental conditions applied.

### 3.2 CH2OO

#### 3.2.1 Linear Fit

For CH2OO a linear fit (i.e. using eqn (E3) vs. H2O) describes the observations well (Fig. 3) over the entire [H2O] range studied (1–20 \(\times 10^{16}\) molecules per cm\(^{-3}\)). This fit gives relative rates \(k_3/k_2\) of 3.3 (±1.1) \(\times 10^{-5}\) and \((k_d + L)/k_2\) of −2.3 (±3.5) \(\times 10^{11}\) cm\(^{-3}\) (Table 2).

These relative rates can be placed on an absolute basis using absolute measurements of \(k_d\)(SCI + SO2). In Table 3 we apply the absolute \(k_d\) values reported by Welz et al.,15 obtained using direct methods at reduced pressure (4 Torr), to the relative rates shown in Table 2. Using this method, the value obtained for \(k_d\)(CH2OO + H2O) is 1.3 (±0.4) \(\times 10^{-15}\) cm\(^{-3}\) s\(^{-1}\). This is consistent with the recent determination by Welz et al.,15 that \(k_3 < 4 \times 10^{-15}\) cm\(^{-3}\) s\(^{-1}\), but is (ca. 14–50 times) greater than the recent estimates of Ouyang et al.16 \((k_3 = 2.5 (±1) \times 10^{-17}\) cm\(^{-3}\) s\(^{-1}\)) and Stone et al.17 \((k_3 < 9 \times 10^{-17}\) cm\(^{-3}\) s\(^{-1}\)).

The derived \((k_d + L)\) value for CH2OO using this method is −8.8 (±13) s\(^{-1}\), i.e. zero within uncertainty. Theoretical work22 has predicted \(k_d\)(CH2OO) to be small (~0.3 s\(^{-1}\)), in agreement with the experimentally derived value reported here.

#### 3.2.2 CH2OO + (H2O)2

Recent experimental work46 has reported the reaction of CH2OO with the water dimer, (H2O)2, (reaction (R5)) to be very fast (1.1 \(\times 10^{-11}\) cm\(^{-3}\) s\(^{-1}\) – assuming \(k_3 = 3.9 \times 10^{-11}\) cm\(^{-3}\) s\(^{-1}\) (ref. 15)), in broad agreement with theoretical predictions,47 but in contrast to other experimental work.15

\[
\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2 \xrightarrow{k_1} \text{products} \quad (R5)
\]

The CH2OO data from this study appear to be well described by a linear fit under the experimental conditions applied (a fast reaction of CH2OO with (H2O)2 would be manifested as a significant upward curvature in Fig. 3). However, this does not mean the results are inconsistent with reaction of CH2OO with (H2O)2.

In Fig. 4, eqn (E4) (an expanded version of eqn (E3), including the SCI + (H2O)2 reaction (R5)) is applied to the data, now expressed in terms of (H2O)2, calculated for each RH via the equilibrium constant:48

\[
[\text{SO}_2]_0 \left( \frac{1}{k_2} - 1 \right) = \frac{k_1}{k_2} \left( \frac{[\text{H}_2\text{O}]_2}{k_p + \frac{k_5}{k_2}([\text{H}_2\text{O}]_2)} \right) + \frac{k_d}{k_2}
\]

The value for \(k_d/k_2\) (water monomer) derived from the fit shown in Fig. 4 is 2.5 (±0.7) \(\times 10^{-5}\). It is seen that this value is rather insensitive to the inclusion of the (H2O)2 term in eqn (E4) as the value is within the uncertainties of the linear fit to the data presented in Fig. 3 – see also Table 2. Converting this value to an absolute value using the \(k_3\) from Welz et al.15 gives \(k_5 = 9.9 (±2.9) \times 10^{-16}\) cm\(^3\) s\(^{-1}\). The derived value of \(k_d/k_3\) is -6.4 (±66) \(\times 10^{-10}\) cm\(^3\) s\(^{-1}\), which, using the Welz et al.15 \(k_5\) gives an absolute value for \(k_5\) of ~1.5 (±16) s\(^{-1}\). This is again indistinguishable from zero, within uncertainty, as is the \(k_d\) determined from eqn (E3) (Fig. 3).

Note the large uncertainties in \(k_d\), resulting from allowing three parameters to vary in the optimisation; consequently \(k_d\) was fixed to zero in eqn (E4) to determine the \(k_5/k_2\) and \(k_3/k_2\) values.

The resulting value of \(k_5/k_2\) (water dimer) is 1.4 (±1.8) \(\times 10^{-2}\). Converting this to an absolute value using the \(k_3\) from Welz et al.15 gives \(k_5 = 5.6 (±7.0) \times 10^{-13}\) cm\(^3\) s\(^{-1}\). This is roughly a factor of twenty smaller than the value derived by Berndt et al.,46 but within a factor of two of the upper limit for \(k_5\) deduced by Welz et al. (<3 \(\times 10^{-13}\) cm\(^3\) s\(^{-1}\)) (ref. 45) from the data presented by Stone et al.17 The inset plot in Fig. 4 also shows two additional fits generated using eqn (E4) with \(k_d/k_3\) fixed to 9.9 \(\times 10^{-16}\) and \(k_d\) fixed to zero. One fit line uses the \(k_5\) value reported by Berndt et al.46 (blue dashed line). This is seen to overestimate the presented data. The green dotted line shows a fit to the upper limits of the uncertainties of the measured data. This yields a \(k_5/k_2\) value of 0.10 (±0.01), giving an upper limit \(k_5\) value of 3.9 (±0.39) \(\times 10^{-12}\) cm\(^3\) s\(^{-1}\).

<table>
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<tr>
<th>SCI</th>
<th>(10^5 k_3/k_2)</th>
<th>(10^{15} k_3) (cm(^3) s(^{-1}))</th>
<th>(10^{-11} k_d/k_2) (cm(^3))</th>
<th>(k_d) (s(^{-1}))</th>
<th>Ref.</th>
<th>Method</th>
<th>Conditions(^a)</th>
</tr>
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<tr>
<td>CH2OO</td>
<td>3.3 (±11)</td>
<td>1.3 (±0.4)(^b)</td>
<td>&lt;4 (±0.9)</td>
<td>−2.3 (±3.5)</td>
<td>−8.8 (±13)(^b)</td>
<td>This work</td>
<td>Ethene ozonolysis</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Welz et al.(^c)</td>
<td>Alkyl iodide photolysis</td>
<td>4 Torr; 298 K</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Stone et al.(^d)</td>
<td>Alkyl iodide photolysis</td>
<td>200 Torr; 295 K</td>
</tr>
<tr>
<td>CH3CHO</td>
<td>26 (±10)</td>
<td>12 (±4.5)(^e)</td>
<td>13 (±43)</td>
<td>59 (±196)</td>
<td>This work</td>
<td>C2B ozonolysis</td>
<td>296–302 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33 (±10)</td>
<td>15 (±4.5)(^f)</td>
<td>−14 (±31)</td>
<td>This work</td>
<td>T2B ozonolysis</td>
<td>297–302 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anti 10 (±4); syn &lt;4</td>
<td></td>
<td>−64 (±141)</td>
<td>Taatjes et al.(^g)</td>
<td>Alkyl iodide photolysis</td>
<td>4 Torr; 298 K</td>
</tr>
<tr>
<td></td>
<td>8.8 (±0.4)</td>
<td>12 (±0.1)</td>
<td></td>
<td>76 (25–228)</td>
<td>Berndt et al.(^h)</td>
<td>T2B ozonolysis</td>
<td>293 K</td>
</tr>
<tr>
<td>(CH3)2CO2</td>
<td>8.7 (±2.5)</td>
<td>2.1 (±0.6)(^i)</td>
<td>63 (±14)</td>
<td>151 (±35)(^l)</td>
<td>This work</td>
<td>TME ozonolysis</td>
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<td></td>
<td>&lt;0.4 (±2.3)</td>
<td>42 (±3)</td>
<td></td>
<td>Berndt et al.(^j)</td>
<td>TME ozonolysis</td>
<td>293 K</td>
</tr>
</tbody>
</table>

\(^a\) Experiments were conducted at atmospheric pressure unless stated otherwise. \(^b\) Assuming \(k_3 = 3.9 \times 10^{-11}\) cm\(^3\) s\(^{-1}\) (Welz et al.\(^c\)). \(^c\) Assuming \(k_3 = 4.55 \times 10^{-11}\) cm\(^3\) s\(^{-1}\). Average of \(k_3\) for syn and anti CH3CHO conformers from Taatjes et al.\(^g\). \(^d\) Assuming \(k_3 = 2.4 \times 10^{-11}\) cm\(^3\) s\(^{-1}\), \(k_d\) for syn-CH3CHO from Taatjes et al.\(^g\).
Fig. 4 Application of eqn (E4) to derive rate constants for reaction of CH3OO with H2O (k_f/k_2 and (H2O)_2 (k_f/k_2) relative to that of CH2OO with SO2. Inset: eqn (E4) as shown in the main figure (red line), (E4) applied using the dimmer reaction rate (k_f) reported by Berndt et al. (1.1 x 10^{-11} cm^3 s^{-1}) (dashed line) and a fit of (E4) to the upper limits of the uncertainties in the ethene data (solid green line).

The contribution of (H2O)_2 to the removal of CH2OO increases in relation to that of H2O as [H2O] increases. Hence at typical atmospheric [H2O] (~2.5-7.5 x 10^{17} molecules per cm^{-3}), greater than was accessible in this study, reaction with (H2O)_2 could become the dominant sink for CH2OO. In this case using just the H2O monomer kinetics in models would considerably underestimate the total effect of water on removal of CH2OO in the atmosphere.

3.3 CH2CHO

3.3.1 Single SCI Approach. The CH2CHO data shown in Fig. 3 for both cis and trans-but-2-ene appear to be well described (within the uncertainties) by a linear fit to eqn (E3), with the exception of the experiment at the highest RH ([H2O] = 1.8-1.9 x 10^{17} cm^{-3}) in both cases. The kinetic parameters derived from the linear fit to the data (Fig. 3), excluding eqn (E3) (which treats the system as producing a single SCI), excluding the highest RH experiments, are shown in Table 2. Very similar results are obtained for k_f/k_2 for CH2CHO derived from both cis- and trans-but-2-ene ozonolysis, with values of 26 (±10) x 10^{-5} and 33 (±10) x 10^{-5} respectively. The (k_d + L)/k_2 obtained for CH2CHO from cis-but-2-ene ozonolysis is 13 (±43) x 10^{11} molecule cm^{-3} and from trans-but-2-ene ozonolysis ~14 (±31) x 10^{11} molecule cm^{-3}. Berndt et al. reported the k_f/k_2 ratio from trans-but-2-ene ozonolysis to be 8.8 (±0.4) x 10^{-5} (also assuming a single SCI system), a factor of 3.75 smaller than that reported there.

The relative rate constants (Table 2) can be placed on an absolute basis using the measurements of k_2(SCI + SO2) reported by Taatjes et al. (derived using the same methodology as for CH2OO) (Table 3). As eqn (E3) treats the SCI produced as a single SCI, we use an average of the syn and anti conformer rates presented in Taatjes et al. 4.55 x 10^{-11} cm^3 s^{-1}. Using this method, the value obtained for k_2(CH2CHO + H2O) from cis-but-2-ene ozonolysis is 12 (±4.5) x 10^{-15} cm^3 s^{-1} and from trans-but-2-ene ozonolysis is 15 (±4.5) x 10^{-15} cm^3 s^{-1}. Taking a mean of the k_2 values reported for the two CH2CHO conformers by Taatjes et al. gives a value of 7.0 x 10^{-15} cm^3 s^{-1}, while Sheps et al. give a mean value of 12 x 10^{-15} cm^3 s^{-1}. The values obtained for (k_d + L) are 59 (±196) s^{-1} from cis-but-2-ene and -64 (±141) s^{-1} from trans-but-2-ene. Clearly there is a large uncertainty associated with the k_2 determined from this analysis. Fenske et al. have reported k_f(CH2CHO) from trans-but-2-ene ozonolysis to be 76 s^{-1} (accurate to within a factor of three).

3.2.2 Two conformer system. In Fig. 1 it is evident that dSO2/dO3 falls rapidly with increasing [H2O] for all but-2-ene experiments as RH is initially increased, but that the experiments at higher RH all appear to display a similar dSO2/dO3, i.e. the trend in decreasing SO2 removal with increasing H2O levels off. From this observation it appears that there may be competing H2O dependencies to the SO2 loss present. This is manifested in Fig. 3 as a curving over of the data at high RH. We propose two possible explanations for this observation: firstly that it arises from differing kinetics of the two CH2CHO conformers formed in but-2-ene ozonolysis; secondly that the behaviour may reflect the presence of an additional oxidant being formed in the ozonolysis system that reacts with SO2 but is less sensitive to H2O. The first of these possibilities is discussed below, the second is discussed in relation to (CH2)2COO in the following section.

One explanation for the observed non-linearity at high RH apparent in Fig. 3 is the differing reactivities of the syn- and anti-conformers of CH2CHO produced in the ozonolysis of cis- and trans-but-2-ene. It has been predicted that the anti-conformer reacts with H2O several orders of magnitude faster than the syn-conformer, while the rate constant for the SCI reaction with SO2 has been determined experimentally to be about a factor of three greater for the anti-conformer than the syn-conformer. The fraction of each conformer that is lost to reaction with SO2 can be considered in the same way as illustrated in eqn (E2), leading to eqn (E5) and (E6) below, plus simplifications outlined in the following text. The total loss of SO2 to CH2CHO is then the sum of the fractional loss to each conformer, multiplied by the relative SCI yield (i.e. φ^{SW}/φ) of that conformer (eqn (E7)).

\[
f^{\text{syn}} = \frac{\phi^{\text{SW}}}{\phi} \frac{\sum [\text{SO}_2]}{[\text{SO}_2] + \frac{k_2}{k_1} [\text{H}_2\text{O}]} \approx \frac{\sum [\text{SO}_2]}{[\text{SO}_2] + \frac{k_2}{k_1} [\text{H}_2\text{O}]}
\]

\[
f^{\text{anti}} = \frac{\sum [\text{SO}_2]}{[\text{SO}_2] + \frac{k_2}{k_1} [\text{H}_2\text{O}]}
\]

\[
f = f^{\text{syn}} + f^{\text{anti}}
\]

Eqn (E8) can then be fitted to the data presented in Fig. 3 for cis- and trans-but-2-ene (Fig. 5).

\[
[\text{SO}_2] (1 - \frac{1}{f}) = \frac{\sum [\text{SO}_2]}{\phi^{\text{SW}} f^{\text{syn}} + f^{\text{anti}} - 1}
\]

Here we make two assumptions to reduce the degrees of freedom and hence make the problem tractable with the
Further theoretical work predicts a rate constant for the uncertainties, suggests that these kinetics, which is indistinguishable from zero within the experimental conditions used. If the kinetics derived from treating the but-2-ene data in Fig. 3 as representing a single SCI are dominated by the anti-conformer then the $k_d$ derived from these kinetics, which is indistinguishable from zero within the uncertainties, suggests that $k_{\text{anti}}^d$ is small. Taatjes et al. report $k_{\text{anti}}^d$ to be 1.0 (±0.4) × 10^{-14} cm^3 s^{-1}, while Sheps et al. report a value of 2.4 (±0.4) × 10^{-14} cm^3 s^{-1}. Thus, even at the lowest $[\text{H}_2\text{O}]$ considered here (∼1 × 10^{16} cm^{-3}), loss of anti-CH$_3$CHOO to H$_2$O would be >100 s$^{-1}$, and decomposition negligible in comparison (including a $k_{\text{anti}}^d$ of 50 s$^{-1}$ changes the derived $k_{\text{anti}}^d$ and $k_{\text{syn}}^d$ values by <5%).

Fitting eqn (E8) to the data shown in Fig. 5 derives a range of values for $k_{\text{anti}}^d$ and $k_{\text{syn}}^d$ dependent on the values of $\gamma_{\text{anti}}$ and $\gamma_{\text{syn}}$ used. As the Cls, once formed and thermalised, are expected to show the same kinetic behaviour in these experiments irrespective of their precursor alkene, the measurements from the cis-but-2-ene and trans-but-2-ene experiments can be used in combination to constrain $k_{\text{anti}}^d$, $k_{\text{syn}}^d$ and also $\gamma_{\text{syn}}$ and $\gamma_{\text{anti}}$ from each alkene. Fig. 6 plots the $k_{\text{anti}}^d$ vs. $k_{\text{syn}}^d$ determined at different $\gamma_{\text{syn}}$ and $\gamma_{\text{anti}}$ from cis-but-2-ene and trans-but-2-ene. Where these two lines intercept represents the unique solution for both $k_{\text{anti}}^d$ and $k_{\text{syn}}^d$ (Table 4).

Fig. 6 determines $k_{\text{anti}}^d/k_{\text{syn}}^d$ to be 3.5 (±3.1) × 10^{-4} and $k_{\text{syn}}^d/k_{\text{anti}}^d$ to be 1.2 (±1.1) × 10^{-13} cm^{-3}. The 2σ uncertainties presented are, unsurprisingly, large as there are two free parameters. Using the relevant values of $k_2$ for the syn and anti-CH$_3$CHOO conformers from Taatjes et al. to place the relative rate constants on an absolute basis gives a value for $k_{\text{anti}}^d$ of 2.3 (±2.1) × 10^{-14} cm$^{-3}$ s$^{-1}$ and for $k_{\text{syn}}^d$ of 288 (±275) s$^{-1}$. This $k_{\text{syn}}^d$ is comparable to (a factor of two greater than) that reported by Taatjes et al. (1.0 (±0.4) × 10^{-14}). Novelli et al. have recently reported $k_{\text{syn}}^d$ to be an order of magnitude smaller (3–30 s$^{-1}$) based on direct observation of OH formation during trans-but-2-ene ozonolysis at atmospheric pressure.

The point of interception in Fig. 6 also determines the relative yields of the two conformers, $\gamma_{\text{syn}}$ and $\gamma_{\text{anti}}$ (which in turn has been used to derive the optimised fits shown in Fig. 5). For cis-but-2-ene these are determined as 0.45 and 0.55 for $\gamma_{\text{syn}}$ and $\gamma_{\text{anti}}$ respectively. For trans-but-2-ene they are determined as 0.25 for $\gamma_{\text{syn}}$ and 0.75 for $\gamma_{\text{anti}}$. The analysis performed in this section has implications for the determination of the SCI yield. Using the relative rate constant $k_3/k_2$ (anti-CH$_3$CHOO) obtained, as shown in Table 4, it is calculated that ∼90% of the anti-CH$_3$CHOO produced in the SCI yield experiments would react with SO$_2$. From the determined $k_3/k_2$ (syn-CH$_3$CHOO) it is calculated that ∼67% of the syn-CH$_3$CHOO produced in the SCI yield experiments would react with SO$_2$. Applying these (with the corresponding syn and anti yields shown in Table 4) corrections to $\phi_{\text{min}}$ determines total SCI yields of 0.29 for trans-but-2-ene and 0.42 for cis-but-2-ene. These values both lie within the uncertainties in the SCI yields presented in Table 1 for the two but-2-ene systems.

It is not practicable to assess the possible contribution of the water dimer to the SCI loss for CH$_3$CHOO because of the
number of free parameters that would result for a small dataset. However, theoretical predictions suggest that this may be less important for CH$_3$CHO than for CH$_2$OO, indicating $k$(H$_2$O)/$k$(H$_2$O) to be two orders of magnitude smaller for anti-CH$_3$CHO than for CH$_2$OO.

### 3.4 (CH$_3$)$_2$COO

#### 3.4.1 Linear fit

For (CH$_3$)$_2$COO a value of 8.7 ($\pm$2.5) $\times$ 10$^{-5}$ (Table 2) was obtained from a linear fit to the data in Fig. 3, excluding the experiment performed at the highest RH ([H$_2$O] = 1.6 $\times$ 10$^{-7}$ cm$^{-3}$) from the regression. $k$(CH$_3$)$_2$COO reported as 63 ($\pm$14) $\times$ 10$^{-11}$ molecule per cm$^{-3}$ s. These values can be placed on an absolute basis using the measurements of $k$(syn-CH$_3$CHO)+SO$_2$ reported by Taatjes et al. as there are no reported $k$ values for (CH$_3$)$_2$CHO from direct experiments and (CH$_3$)$_2$COO is a syn-conformer (i.e. there is always a methyl group in a syn orientation to the terminal oxygen). This gives values for $k$(CH$_3$)$_2$COO + H$_2$O) of 2.1 ($\pm$0.6) $\times$ 10$^{-15}$ cm$^3$ s$^{-1}$ and for $k$ of 151 ($\pm$35) s$^{-1}$ (Table 3).

Berndt et al. have recently reported the $k$/$k$ ratio for (CH$_3$)$_2$CHO to be $<0.4$ $\times$ 10$^{-5}$ (i.e. approximately a factor of 22 lower than the relative rate reported in this study). Theoretical predictions also suggest $k$ to be very slow, 3.9 $\times$ 10$^{-17}$ cm$^3$ s$^{-1}$. No measured values have been reported for $k$ (CH$_3$)$_2$COO), but a more facile overall decomposition than for CH$_2$OO or the mean of the CH$_3$CHO isomers might be anticipated as the vinylhydroperoxide isomerisation channel is always available.

#### 3.4.2 Additional oxidant

In the case of the SCI formed from TME ozonolysis, (CH$_3$)$_2$COO, there is always a methyl group in a syn position to the carbonyl oxide moiety, thus the analysis presented in Section 3.3.2 for the CH$_3$CHO isomers does not apply. A possible alternative explanation for the observed behaviour (and possible contributor to the behaviour observed in the but-2-ene systems) is that there is a further oxidant (X) of SO$_2$ in addition to the SCI, being formed during the ozonolysis reaction. If this oxidant reacts relatively slowly with H$_2$O, it could give rise to the apparent ‘two component’ nature of the observations seen in Fig. 3. It may also provide an alternative explanation of the observed nature of the SO$_2$ loss from the but-2-ene experiments or could be occurring in addition to the effects of differing conformer reactivities.

Eqn (E9) below is an expanded version of (E2), in which we consider the contribution from a second SO$_2$ oxidant, making the approximation that this species does not react appreciably with water vapour. In eqn (E9), $f$ is the sum of $f$ (the fraction of SCI reacting with SO$_2$) and $f$ (i.e. SCI + X) $\gamma$SCI and $g$. Following the assumption of negligible H$_2$O reactivity, (dSO$_2$/dO$_3$)$_e$ in eqn (E9) can be derived from the SO$_2$ loss at the highest RH experiments (i.e. when all the SO$_2$ loss is attributed to X + SO$_2$) of $\sim$ 10 ppbv. Therefore, loss of SO$_2$ from reaction with X, relative to the loss of O$_2$ (dSO$_2$/dO$_3$)$_e$ is approximately 0.025. $\varphi$ represents the total oxidant yield (i.e. $\phi$SCI + $\phi$). Assuming that $\varphi$ is not dominant ($<0.5$), then $\varphi$ as calculated from correcting $\phi$ to as in Section 3.1, changes little (0.31–0.34) from the value presented in Table 1. Eqn (E10) is then an expanded version of eqn (E3) that includes the additional oxidant term.

$$f = \gamma_{SCI} + \varphi' = \gamma_{SCI} + \frac{1}{\phi} \left( \frac{dSO_2}{dO_3} \right)_x$$

$$[SO_2] \left( \frac{1}{\varphi} - 1 \right) = [SO_2] \left[ \left( \frac{\gamma_{SCI}[SO_2]}{[SO_2] + \frac{k_1}{k_2}[H_2O] + \frac{k_3}{k_2}} + \frac{1}{\phi} \left( \frac{dSO_2}{dO_3} \right)_x \right) - 1 \right]^{-1}$$

Fig. 7 shows eqn (E10) fitted to the TME data from Fig. 3. It is not possible to determine unique values for the parameters included in eqn (E10) due to the degrees of freedom vs. the limited data set. The fit shown in Fig. 7 uses values of $\varphi' = 0.34$, $\gamma_{SCI} = 0.88$, $k_3/k_2 = 6.7 \times 10^{-4}$ and $k_3/k_2 = 1.2 \times 10^{-12}$ cm$^{-3}$. However, Fig. 7 does demonstrate that a two-oxidant system, as represented by eqn (E10), is able to describe the data within uncertainty.

Fig. 7 also includes a linear fit (i.e. eqn (E3)) to the full (CH$_3$)$_2$COO dataset (including the highest RH experiment). While it seems unlikely that the curvature observed in the data is a result of measurement error (as described in Section 3.1), this must be considered as a possibility for (CH$_3$)$_2$COO in light of the two conformer explanation not being applicable. The linear fit in Fig. 7 gives a $k_3/k_2$ value of $3.8 (\pm 3.2) \times 10^{-5}$ cm$^3$ s$^{-1}$, a factor of two smaller than the $k_3/k_2$ value presented in Table 2.

### Table 4 Kinetic parameters derived for syn-CH$_3$CHO and anti-CH$_3$CHO from two-component fits to the trans-but-2-ene (T2B) and cis-but-2-ene (C2B) experiments (see Fig. 5). Also relative ($\varphi$) and absolute ($\varphi$) yields of the two conformers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_1/k_2$</th>
<th>$10^{14} k_3$ (cm$^3$ s$^{-1}$)</th>
<th>$10^{-13} k_1/k_2$ (cm$^{-3}$)</th>
<th>$k_d$ (s$^{-1}$)</th>
<th>T2B</th>
<th>C2B</th>
<th>T2B</th>
<th>C2B</th>
<th>Ref.</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn</td>
<td>—</td>
<td>—</td>
<td>1.2 ($\pm$1.1)</td>
<td>288 ($\pm$275)</td>
<td>0.25</td>
<td>0.45</td>
<td>0.07</td>
<td>0.17</td>
<td>This work</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>($&lt;$0.4)</td>
<td>0.75</td>
<td>0.55</td>
<td>0.21</td>
<td>0.21</td>
<td></td>
<td>This work</td>
<td>—</td>
</tr>
<tr>
<td>C2B</td>
<td>3.5 ($\pm$3.1)</td>
<td>2.3 ($\pm$2.1)</td>
<td>1.0 ($\pm$0.4)</td>
<td>2.4 ($\pm$0.4)</td>
<td>20 (3–30)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\gamma_{syn} = \varphi_{syn}/\varphi$. Experiments were conducted at atmospheric pressure unless stated otherwise and temperatures from 293 to 303 K.
The most obvious candidate for an additional oxidant present to consume SO$_2$ is OH. OH radicals are produced in the chamber, primarily (in the absence of sunlight and NO$_x$) through the alkene + ozone reaction.$^{11}$ However cyclohexane was added in excess at the beginning of each experiment to act as an OH scavenger, such that SO$_2$ reaction with OH was calculated to be \( \leq 1\% \) of the total observed chemical SO$_2$ removal in all experiments. Other potential candidates for this oxidant species include the (stabilised) vinyl hydroperoxide (VHP) intermediate, a secondary ozonide (formed through an SO$_2$–SCI cyclic adduct), and dioxirane (Scheme 1).

Drozd \textit{et al.}$^{10}$ have presented evidence for substantial VHP stabilisation (derived from the (CH$_3$)$_2$COO CI) at pressures of a few hundred Torr, with a lifetime of the order of a few hundred milliseconds with respect to decomposition to form OH, providing scope for bimolecular reactions of this species to occur. This would be consistent with the kinetic observations presented here: a small yield in the systems with syn-SCIs, while for ethene, no VHP intermediate is available, and the standard chemistry ((R1)–(R4)) can be used to satisfactorily reproduce the observations. However, no significant SO$_2$ reactivity is known for the peroxide or alkene functionalities present in the closed shell VHP in isolation, hence it may be surprising if this species reacted rapidly with SO$_2$, although theoretical studies have suggested that the VHP may react with H$_2$O.$^{23}$

Secondary ozonide species, formed as an adduct from the SCI + SO$_2$ reaction, have been suggested to account for the observed isotopic exchange in alkene–ozone–SO$_2$ systems,$^{25}$ and are suggested to have lifetimes of seconds or longer.$^{10}$ Such a secondary ozonide could react with a further SO$_2$ molecule (i.e. a two-component secondary ozonide catalysed oxidation route for SO$_2$ to SO$_3$ conversion), however a substantial humidity dependence to the overall process may still be anticipated (on the basis of SCI removal through the SCI + H$_2$O reaction), which is not shown here.

The ‘hot acid/ester channel’ (rearrangement and decomposition via a dioxirane intermediate) is the dominant isomerisation route available for anti-SCIs. Although the hydroperoxide channel is the principal isomerisation route for syn-SCIs, the ester mechanism is also available,$^{25}$ and it is likely that a small proportion of the syn-SCI will isomerise through this channel to form a dioxirane. Dioxiranes are known to be highly reactive and selective oxidising agents,$^{51,52}$ and have a particular affinity for sulphur compounds.$^{53}$ Additional oxidation of SO$_2$ by the dioxirane, over and above that arising directly from reaction with the SCI, could then explain the observed behaviour of SO$_2$ in the TME experiments (and contribute to the behaviour observed for the but-2-ene systems). For the small CI CH$_3$OO, formed in the ethene system, it has been predicted that the dioxirane formed is considerably less stable than the methyl substituted dioxiranes formed from but-2-ene and TME ozonolysis, and furthermore will decompose promptly due to chemical activation.

The possibility of non-CI products of the ozonolysis system being responsible for some of the observed SO$_2$ oxidation has been suggested previously as an alternative (or additional) explanation for the observed behaviour of SO$_2$ in the atmosphere.$^{1,54,55}$ In their laboratory study Berndt \textit{et al.}$^{19}$ note that their data were not perfectly described by a model in which a single (SCI related) SO$_2$ oxidation process was assumed, and commented that the SO$_2$ oxidation in ozonolysis systems may in fact be more complex. Taatjes \textit{et al.}$^{56}$ have recently suggested that these data$^{19}$ are consistent with a two-component oxidation system, either two processes removing SO$_2$ in parallel (as described above), or through a sequential two-step SO$_2$ removal mechanism, such as the secondary ozonide route outlined above. However, this latter mechanism cannot (in isolation) account for the observations presented here.

The presence of an additional oxidant would have implications for the role of alkene ozonolysis in oxidation of trace gases in the atmosphere. If an oxidant is being formed that reacts slowly with H$_2$O then this, perhaps in addition to SCI, may contribute to the additional (non-OH) SO$_2$ oxidation observed in recent field experiments.$^1$ Further investigation of this possibility is needed.

As for CH$_3$CHO, the analysis performed in this section has implications for the determination of the SCI ((CH$_3$)$_2$COO) yield. Using the value of $k_4$ derived from the linear fit to all the data shown in Fig. 7 would indicate an SCI yield of 0.33. Using the value of $k_4$ derived from the ‘additional oxidant fit in Fig. 7, and taking into account that \( \sim 10 \) ppb of the SO$_2$ loss in the high SO$_2$ experiment would be attributed to reaction with the additional oxidant rather than the SCI, determines a slightly lower $q_{\text{min}}$ of 0.23, and a corrected yield of 0.32, very similar to that shown in Table 1. Both of these possible alternative SCI yields lie within the uncertainties in the SCI yield from TME ozonolysis presented in Table 1.

As for CH$_3$CHO, it is not possible to quantitatively consider the contribution of the water dimer to the SCI loss given the limited data, but theory$^{53}$ predicts $k$(H$_2$O)$_2$/$k$(H$_2$O) to be three orders of magnitude smaller than that for CH$_3$OO suggesting that reaction with the water dimer would be unimportant for (CH$_3$)$_2$COO at typical atmospheric boundary layer [H$_2$O].

4. Atmospheric implications

The derived values for $k_3$ reported in Table 3 correspond to loss rates for reaction of SCI with H$_2$O in the atmosphere of 650 s$^{-1}$ for CH$_3$OO, \( \sim 3500 \) s$^{-1}$ for CH$_3$CHO, and \( \sim 1050 \) s$^{-1}$ for (CH$_3$)$_2$COO.
(assuming [H₂O] = 5 × 10¹⁷ molecules per cm⁻³, equivalent to an RH of 65% at 298 K). Comparing this to the derived kₙ values it is seen that reaction with H₂O is predicted to be the main sink for SCI in the atmosphere, but also that loss through decomposition cannot be neglected for some SCI – contributing on the order of 0–1% for CH₃CHO and 13% for (CH₃)₂COO.

An estimate of a mean steady state SCI concentration in the background atmospheric boundary layer can then be calculated using eqn (E11).

\[
[\text{SCI}] = \frac{[\text{Alkene}][O₂]k_{\text{f}}\phi}{k_{\text{h}}[\text{H₂O}] + k_{\text{d}}} \quad (E11)
\]

Using the data given below, a steady state SCI concentration of 1.7 × 10³ molecules per cm⁻³ is estimated for an ozonolysis source (noting that other potential atmospheric sources of SCI exist, e.g. photolysis of alkyl-iodides in the marine boundary layer, and sinks, e.g. reaction with NO and NO₂). This assumes an ozone mixing ratio of 40 ppbv, an alkene mixing ratio of 2 ppbv, \(\phi\) of 0.35, and mean reaction rate constants \(k_{\text{h}}\) (alkene–ozone) of 1 × 10⁻¹⁶ cm³ s⁻¹; \(k_{\text{d}}\) (SCI + SO₂) of 3.5 × 10⁻¹¹ cm³ s⁻¹, \(k_{\text{i}}\) (SCI + H₂O) of 2 × 10⁻¹⁵ cm³ s⁻¹, \(k_{\text{d}}\) of 30 s⁻¹ with [H₂O] of 5 × 10¹⁷ cm⁻³ (RH ~ 65%).

However, in the case of CH₃CHO the data shown in Fig. 3, and the discussion above, indicate contributions from multiple species – syn- and anti-conformers with contrasting behaviour. It is clear that the burden of CH₃CHO in the atmosphere would be better described by considering these two fractions of SO₂ loss separately. Eqn (E12) expands eqn (E11) to treat the two conformers separately, where \([\text{SCI}] = [\text{anti-SCI}] + [\text{syn-SCI}]\), making the same assumptions as for the analysis of CH₃CHO in eqn (E5) and (E6). \(k_{\text{anti}}\) is estimated to be 1 × 10⁻¹⁴ cm³ s⁻¹ (taking into account that CH₂OO is considered as an anti-SCI in this analysis and that the derived \(k_{\text{i}}\) (CH₃OO) is more than an order of magnitude smaller than the derived \(k_{\text{i}}\) (CH₃CHO) of 2.3 × 10⁻¹⁴ cm³ s⁻¹), \(k_{\text{syn}}\) is assumed to be 200 s⁻¹ and \(\phi_{\text{anti}} = \phi_{\text{syn}} = 0.175\). Additionally the anti-SCI + water dimer reaction is also considered, using a value of 5.6 × 10⁻¹³ cm³ s⁻¹ as derived for CH₂OO in this work.

\[
[\text{SCI}] = [\text{Alkene}][O₂]k_{\text{f}}\left(\frac{\phi_{\text{anti}}}{k_{\text{antih}}[\text{H₂O}] + k_{\text{d}}^\text{anti}K_p[H₂O]^2} + \frac{\phi_{\text{syn}}}{k_{\text{synh}}}ight) \quad (E12)
\]

Using these values in eqn (E12) determines \([\text{anti-SCI}] = 164\) molecules per cm⁻³ and \([\text{syn-SCI}] = 4.4 \times 10^3\) molecules per cm⁻³. The formation of an additional oxidant during alkene ozonolysis would be expected to have a similar effect to the two component contribution presented in eqn (E12) based on the apparent yields from the experiments presented here. From this analysis the atmospheric SCI burden is seen to likely be dominated by syn-SCI since this term is at least an order of magnitude greater than the anti-SCI term.

A typical diurnal loss rate of SO₂ to OH (\(k_{\text{OH}} \times [\text{OH}]\)) is 9 × 10⁻⁷ s⁻¹, while the SO₂ loss rate due to reaction with SCI, using the values derived from eqn (E12), would be 1.2 × 10⁻⁷ s⁻¹. This suggests, for the conditions and assumptions given above, the loss of SO₂ to SCI to be about 13% of loss to OH. This analysis neglects additional chemical sinks for SCI, which would reduce SCI abundance but are unlikely to be competitive with the two main SCI loss processes identified herein. SCI concentrations are expected to vary greatly depending on the local environment, e.g. alkene abundance may be considerably higher (and with a different reactive mix of alkens) in a forested environment, compared to a rural background environment. The majority of the SCI burden, particularly in forested regions, is likely to be dominated by SCI derived from (C₅) isoprene and (C₁₀) monoterpenes. The chemistry of these species could differ greatly from the small SCI reported here (which we have found to be structure specific, even for small alkene systems), especially for tethered SCI derived from ozonolysis of internal double bonds within (for example) some monoterpenes. It is clear that the total SCI loss rate is dependent upon SCI identity and configuration, and that further work is required to quantify speciated SCI in the atmosphere, and to accurately calculate SCI concentrations for use in atmospheric modelling.

5. Conclusions

It has been shown that at relatively low [H₂O] (<1 × 10¹⁷ cm⁻³) the loss of SO₂ in the presence of four ozone–alkene systems; ethene, cis-but-2-ene, trans-but-2-ene and 2,3-dimethyl-but-2-ene significantly decreases with increasing water vapour. This is consistent with production of a stabilised Criegee intermediate from the ozonolysis reaction and subsequent reaction of this species with SO₂ and H₂O. Competition between H₂O and SO₂ for reaction with the SCI leads to the observed relationship which is sensitive to water vapour abundance over a relatively narrow range of RH. Derived kinetic data for these ozonolysis systems shows that the reaction rates are dependent on the structure of the SCI. At [H₂O] > 1 × 10¹⁷ cm⁻³ the SO₂ loss in the presence of cis- and trans-but-2-ene, and 2,3-dimethyl-but-2-ene appears to show a reduced dependence upon H₂O. The results suggest that there is an H₂O dependent and an H₂O independent fraction to the observed SO₂ loss in these systems. These two fractions may be attributable to differing kinetics of the two conformers produced in but-2-ene ozonolysis or to other oxidant products of the alkene ozonolysis reaction. This observation means that SCI structure must be considered in atmospheric modelling of SCI production from alkene ozonolysis, and suggests that the atmospheric SCI burden (and hence the oxidation of trace gases) will be dominated by syn-SCI.

This work provides constraints on the behaviour of SCI formed through alkene ozonolysis under conditions relevant to the atmospheric boundary layer, but also highlights the complex nature and incomplete current understanding of the ozonolysis system. Further research is needed to definitively quantify the impact of this chemistry upon atmospheric oxidation.

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Notes and references

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