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# PAPER

### Total radical yields from tropospheric ethene ozonolysis†

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The gas-phase reactions of ozone with alkenes can be significant sources of free radicals (OH, HO<sub>2</sub> and RO<sub>2</sub>) in the Earth's atmosphere. In this study the total radical production and degradation products from ethene ozonolysis have been measured, under conditions relevant to the troposphere, during a series of detailed simulation chamber experiments. Experiments were carried out in the European photoreactor EUPHORE (Valencia, Spain), utilising various instrumentation including a chemical-ionisation-reaction time-of-flight mass-spectrometer (CIR-TOF-MS) measuring volatile organic compounds/oxygenated volatile organic compounds (VOCs/OVOCs), a laser induced fluorescence (LIF) system for measuring HO<sub>2</sub> radical products and a peroxy radical chemical amplification (PERCA) instrument measuring HO<sub>2</sub> +  $\Sigma$ RO<sub>2</sub>. The ethene + ozone reactions system was investigated with and without an OH radical scavenger, in order to suppress side reactions. Radical concentrations were measured under dry and humid conditions and interpreted through detailed chemical chamber box modelling, incorporating the Master Chemical Mechanism (MCMv3.1) degradation scheme for ethene, which was updated to include a more explicit representation of the ethene–ozone reaction mechanism.

The rate coefficient for the ethene  $\pm$  ozone reaction was measured to be  $(1.45 \pm 0.25) \times 10^{-18}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298 K, and a stabilised Criegee intermediate yield of  $0.54 \pm 0.12$  was determined from excess CO scavenger experiments. An OH radical yield of  $0.17 \pm 0.09$  was determined using a cyclohexane scavenger approach, by monitoring the formation of the OH-initiated cyclohexane oxidation products and HO<sub>2</sub>. The results highlight the importance of knowing the [HO<sub>2</sub>] (particularly under alkene limited conditions and high [O<sub>3</sub>]) and scavenger chemistry when deriving radical yields. An averaged HO<sub>2</sub> yield of  $0.27 \pm 0.07$  was determined by LIF/model fitting. The observed yields are interpreted in terms of branching ratios for each channel within the postulated ethene ozonolysis mechanism.

### 1. Introduction

Methyl-substituted ethenes ( $C_2$ – $C_6$ ) are emitted to the atmosphere from a wide range of sources, which include combustion processes and vehicle emissions. They are significant primary pollutants in the boundary layer, contributing to the total volatile organic compound (VOC) emissions in urban air. Unsaturated VOCs may account for up to 30% of the total OH sink<sup>1</sup> and can contribute significantly to ozone formation

in urban environments.<sup>2</sup> However, another key fate for alkenes is reaction with ozone, which may form the dominant loss pathway depending on local conditions and the time of day.<sup>3</sup> Alkene ozonolysis leads to the production of a wide range of functionalized oxygenated products, including carbonyls, organic acids and hydroperoxides, and also serves as a non-photolytic source of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals.<sup>1,4</sup> In addition, the gas-phase ozonolysis of biogenic alkenes, notably C10 monoterpenes and C15 sesquiterpenes, is known to lead to the production of semi-volatile oxygenated compounds that have been detected in secondary organic aerosol (SOA).<sup>5,6</sup> General mechanistic details for the reactions of simple unsaturated hydrocarbons with ozone are thought to be relatively well known. However, there are quantitative details of the reaction pathways that need to be determined in order to accurately understand their implications for the atmosphere.<sup>7</sup> The role of alkene ozonolysis reactions in the tropospheric  $HO_x$  (OH + HO<sub>2</sub>) budget has been established by a number of studies (ref. 3 and 7 and refs within). For example, during both urban and rural case studies in Los Angeles and a forested site in Alabama,

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it was illustrated that, under certain conditions, alkene ozonolysis can be the predominant  $HO_x$  source.<sup>3</sup> In an investigation of the chemistry occurring in a forested region of north-western Greece, observationally constrained box model simulations show the significance of the ozonolysis of biogenics as an important OH source.8 Under polluted urban conditions, alkene ozonolysis accounted for 46% of the daytime radical production in the summer and 62% during winter at an urban site in Birmingham, UK.9 More recently, alkene ozone reactions were reported to be indirectly responsible for 33% of the peak radical production found during the day in Mexico City<sup>10</sup> and, under summertime conditions in Santiago de Chile, contributed  $\sim 24\%$  to the total daytime primary OH radical source.<sup>11</sup> The radical formation potential from the ozonolysis of unsaturated hydrocarbons is therefore of significant interest as it has a substantial influence on the  $HO_x$ budget in both urban and rural environments.<sup>1,3</sup>

Ethene (ethylene,  $H_2C = CH_2$ ), the simplest alkene, is widely used in industry, where it is an important precursor to a wide variety of other organic chemicals. In terms of its mass emission, ethene is one of the most significant VOCs released into the environment, found in urban atmospheres at up to parts per billion (ppbV) levels.<sup>2,12</sup> It has been estimated that exposure to as little as 10 ppbV of ethene for one hour each week may lead to an increased lifetime risk of cancer amounting to approximately 70 per 100 000 persons.<sup>13</sup> In terms of the ozonolysis reaction mechanism, the simple structure of ethene means that its reaction with ozone is unique, in that it cannot follow OH production via the hydroperoxide mechanism.<sup>7</sup> The carbonyl oxide [CH2OO]\* (also known as a Criegee intermediate),<sup>14</sup> formed from ethene ozonolysis is also a product formed from the ozonolysis of all terminal alkenes, including the important monoterpenes β-pinene and limonene, as well as isoprene, the dominant non-methane hydrocarbon emitted into the atmosphere. Understanding of the fate and kinetics of the gas-phase reaction between ethene and ozone therefore underpins interpretation of experimental measurements of radical production from biogenic alkene ozonolysis.

Gas-phase ethene ozonolysis is believed to proceed via the Criegee mechanism,<sup>14</sup> illustrated in Fig. 1. Ozonolysis is initiated by a concerted electrophilic 1,3-cycloaddition of ozone across the double bond to form a primary ozonide (POZ) (1a). This intermediate is high in energy and rapidly decomposes, giving rise to a vibrationally excited carbonyl oxide and a stable (primary) carbonyl molecule, formaldehyde in the case of ethene. The carbonyl oxide [CH2OO]\*, hereafter referred to as a Criegee intermediate (CI), has often been referred to as carbonyl oxide, dioxymethylene or peroxymethylene biradical, owing to its zwitterionic/biradical electronic structure. However, ab initio calculations have indicated that the ground state of the [CH<sub>2</sub>OO]\* CI is not the zwitterion, and may be regarded simply as a biradical,<sup>15–17</sup> as illustrated in Fig. 1. The carbonyl and CI co-products produced from the exothermic decomposition of the POZ (1b) possess a significant amount of vibrational excitation, enabling further unimolecular reactions of the excited CI to occur (but the energy involved is not sufficient for the decomposition of the carbonyl compound to occur). Potential fates of the CI include: direct rearrangement and decomposition via a four-membered transition state

(reaction 2 in Fig. 1), rearrangement through a dioxirane structure (reaction 3), which can decompose to various products (3a-3d), possibly via a 'hot' acid intermediate, or stabilisation (reaction 4) followed by bimolecular reactions, e.g. 4a-4c. The syn-mono and di-methyl substituted CI's are thought to decompose predominantly through isomerisation via a fivemembered transition state to give an excited hydroperoxide species which subsequently decomposes to give OH and a vinoxy radical.<sup>7</sup> However, even in the absence of the so called "hydroperoxide" mechanism, OH production is observed, with the decomposition/isomerisation channels 2 and 3a postulated as the likely sources. There are a number of quantitative indirect OH yield measurements from ethene ozonolysis available in the literature, obtained through the use of radical tracer<sup>18,19</sup> and scavenger<sup>20,21</sup> species, plus direct observations reported at pressures between 10–60 Torr and at short timescales  $(ca. 10 \text{ ms}).^{22,23}$  Such direct observations are challenging, as the rate coefficient for the ethene + ozone reaction  $(1.59 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{24}$  is substantially slower than that for other alkenes (e.g. ca. 2 orders of magnitude slower than *cis/trans*-2-butene).<sup>24</sup> This, coupled to the low OH vield, results in a low steady state [OH] which is difficult to observe directly. The high barrier to reaction calculated for channel 2,<sup>25</sup> together with pressure independent OH yields,<sup>26</sup> leads to the hypothesis that it is the fragmentation of the 'hot' acid (3a) that is the dominant source of OH, rather than formation via the four-membered transition state (2).

The current recommended OH yield from ethene ozonolysis at atmospheric pressure is 0.16.24 Measurements of HO<sub>2</sub> and/or potential RO<sub>2</sub> production, however, are scarceproduction of these contributors to  $HO_x$  (which have a similar impact to direct OH production, as much ethene oxidation occurs in moderate to high NO<sub>x</sub> environments with rapid NO-mediated radical cycling) is uncertain. Recently, HO<sub>2</sub> radical measurements from ethene ozonolysis have been performed using matrix isolation with electron spin resonance (MI-ESR)<sup>27</sup> and peroxy radical chemical amplification (PERCA),  $^{28,29}$  with yields of 0.39  $\pm$  0.03 and 0.38  $\pm$  0.02 respectively reported at atmospheric pressure, a factor of 3 greater than those inferred from indirect studies.<sup>24</sup> Radical yields have also been indirectly inferred for a range of alkenes, from long-duration (24-48 h) experiments performed in the SAPHIR chamber;<sup>30</sup> yields of 0.00  $\pm$  0.05 for OH, and  $0.50 \pm 0.25$  for HO<sub>2</sub> were determined from C<sub>2</sub>H<sub>4</sub> and O<sub>3</sub> temporal profiles (with and without a radical scavenger present). with indications that the radical yields may be dependent upon humidity. The production of H atoms has also been reported (in the absence of O<sub>2</sub>) with a yield of  $0.076 \pm 0.060^{31}$  (at 5 Torr), which may result from the decomposition of the formyl radical (HCO) formed via channels 2 and 3a and/or via the 'hot' acid channel (3b). Currently, atmospheric mechanisms (e.g. the Master Chemical Mechanism-MCM) employ yields which are largely inferred through the observation of associated stable products using assumed mechanisms.<sup>32,33</sup> The MCM (MCMv3.1, http://mcm.leeds.ac.uk/MCM/) uses a value of 0.13 for both OH and HO<sub>2</sub> yields, similar to the earlier OH yield recommendation of 0.12.34

In this paper we present the results of a detailed study of ethene ozonolysis, performed under tropospherically relevant



Fig. 1 Schematic representation of the ethene ozonolysis reaction system. Adapted from ref. 4 and 7.

conditions and as a function of humidity, in a large atmospheric simulation (smog) chamber, the EUropean PHOto-REactor, EUPHORE. HO<sub>2</sub> and HO<sub>2</sub> +  $\Sigma$ RO<sub>2</sub> were observed using laser induced fluorescence (LIF) and peroxy radical chemical amplification (PERCA) techniques, respectively. These observations, from experiments with/without radical scavengers employed, together with measurements from a suite of other instrumentation, were then used to derive yields for stable and radical products (from the fast ozonolysis process: CI formation and decomposition) using a detailed chemical mechanism based upon the MCM to account for the subsequent and secondary chemical reactions. We then interpret these yield

data to derive branching ratios for the various channels in the reaction mechanism. Finally, a discussion comparing our results with the existing literature and associated atmospheric implications is presented.

#### 2. Experimental

## 2.1 European photoreactor facility (EUPHORE) and instrumentation

The ethene ozonolysis experiments were carried out in the European Photoreactor Facility (EUPHORE) in Valencia,

Spain as part of the TRAPOZ (Total RAdical Production and degradation Products from alkene OZonolysis) project. EUPHORE is a large scale atmospheric simulation chamber, which is used extensively for studying the mechanisms of photochemical atmospheric processes. More in depth details of the chamber and its instrumentation are given elsewhere.<sup>35,36</sup> Briefly, it consists of two 197 m<sup>3</sup> simulation chambers, formed from fluorine-ethene-propene (FEP) Teflon foil (127 µm thickness) fitted with housings that exclude ambient light. The chamber is fitted with large horizontal and vertical fans to ensure rapid mixing. In this study a range of analytical instruments was used (Table 1) including a laser induced fluorescence (LIF) system for the direct measurement of HO<sub>x</sub> radicals.<sup>37,38</sup> In addition, a peroxy radical chemical amplifier (PERCA)<sup>39</sup> and a chemical ionisation reaction timeof-flight mass-spectrometer (CIR-TOF-MS)<sup>40</sup> were deployed for the measurement of HO<sub>2</sub> +  $\Sigma$ RO<sub>2</sub> and volatile organic/ oxygenated volatile organic compounds (VOCs/OVOCs), respectively.

#### 2.2 Experimental approach

All experiments were performed with the chamber housing closed (*i.e.* dark conditions,  $i(NO_2) < 2 \times 10^{-6} \text{ s}^{-1}$ ), at near atmospheric pressure and ambient temperature, and conducted under  $NO_x$ -free conditions. In the absence of  $NO_x$  and sunlight, chamber wall radical production has been shown to be negligible.<sup>41</sup> For most experiments, humidity was low (in simulation chamber terms: dew point ca. -45 °C/75 ppmV H<sub>2</sub>O). The experimental procedure, starting with a clean flushed chamber, was to add  $SF_6$ (as a dilution tracer), followed by ozone (250-500 ppbV) and in certain cases an OH scavenger (CO or cyclohexane, in concentrations such that  $\geq 95\%$  of any OH produced was scavenged). To initiate the reaction, a known aliquot of ethene (250-500 ppbV) was injected into the chamber. The evolution of reactants and products was then monitored (Table 1) over timescales of 1-3 hours. The chamber mixing time was of the order of 2-3 minutes.

Four types of ozonolysis experiments were carried out: (a) simple,  $C_2H_4/O_3$ : designed to produce OH, HO<sub>2</sub> and potentially RO<sub>2</sub> radicals. OH radicals were near-exclusively removed (chemically) by reaction with ethene, whereas HO<sub>2</sub> and RO<sub>2</sub>

 Table 1 Experimental techniques used during this work<sup>a</sup>

Instrumentation	Target species
Laser Induced Fluorescence (LIF)	OH, HO <sub>2</sub>
Peroxy Radical Chemical Amplifier (PERCA)	$(HO_2 + \Sigma RO_2)$
Fourier Transform Infra Red Spectroscopy,	$C_{2}H_{4}, O_{3}, $
Nicolet Magna 550 (FT-IR)	HCHO, $SF_6$
Chemical ionisation Reaction Time-of-flight	VOCs/OVOCs
Mass Spectrometer (CIR-TOF-MS)	,
High Performance Liquid Chromatography	Hydroperoxides
UV/FLD (HPLC)	• · ·
Nitric Oxide(s) Analyser, CLD770	NO, NO <sub>2</sub> , NO <sub>2</sub>
(chemiluminescence/photolytic NO <sub>2</sub> )	, 2, ,
Ozone Analyser ML9810 (UV absorption)	O3
CO Analyser TE48C (Hantzsch reaction)	CO
Dew Point Hygrometer, Walz	H <sub>2</sub> O
HCHO Analyser AL4001	нсно

<sup>*a*</sup> Radical and compound specific measurement uncertainties and instrument accuracies are discussed in detail in Section 2.3.

were removed by cross- and self-reaction. (b) Excess CO,  $C_2H_4/O_3/CO$ : designed to convert OH to HO<sub>2</sub> by reaction with excess CO.<sup>21</sup> This allowed the total (sum of) OH and HO<sub>2</sub> production to be monitored via measurement of HO<sub>2</sub>, and simplified the interpretation of RO<sub>2</sub> data, as any OH produced from ethene ozonolysis was scavenged by CO, suppressing side reactions. HO<sub>2</sub> removal was therefore dominated by self-reaction. Additionally, the stabilised Criegee intermediates (SCIs) were also effectively scavenged by CO to form HCHO and CO2.42 (c) Excess cyclohexane, C2H4/O3/c-C6H12: designed to obtain an indirect OH yield by monitoring products formed from the OH + cyclohexane reaction,<sup>43</sup> (as the steady state [OH] from ethene ozonolysis was below the detection limit of the LIF system (ca.  $5 \times 10^5$  molecules cm<sup>-3</sup>). (d) Increased humidity: experiments (a) and (b) were performed with graduated addition of water to the chamber, to examine the humidity dependence of the radical yields and the effect of the  $SCI + H_2O$  reaction.

#### 2.3 Instrumental accuracy

The results reported in this study were derived using a range of measurement instrumentation (Table 1). Ozone was monitored by both FT-IR and UV-absorption spectroscopy; the two methods were in very good agreement. CO was measured using a commercial IR monitor; the levels observed were in good agreement with those calculated from the quantities admitted to the chamber. Ethene was monitored by FT-IR with the measurement accuracy limited by the uncertainty of the reference cross sections available and fitting process, conservatively estimated to be 10%. Chamber dilution significantly affects the ethene and ozone time profiles (  $\sim 60\%$ of the ethene loss is due to dilution), but is well constrained by the measured first order decay of  $SF_6$  (as monitored by the FT-IR). HCHO was monitored by FT-IR, CIR-TOF-MS and a formaldehyde monitor (Aerolaser; Hantzsch reaction); the data from all techniques were in good agreement-as the FT-IR beampath traverses the chamber, while the monitor and CIR-TOF-MS sampled from a single point, this served to confirm that the reactants were well mixed (on the timescale of the ethene-ozone decay).

The CIR-TOF-MS was calibrated after the experiments using a variety of methods, these included: (i) for cyclohexanone, direct admission of a known gas standard (BOC Special Gases, UK) to the instrument inlet line, following dynamic dilution (calibration accuracy = 20%); (ii) sampling of "in-house" calibration material produced by the volumetric dilution and liquid injection of cyclohexanone (Sigma Aldrich, purity  $\geq 99\%$ ) into Tedlar sample bags (calibration accuracy = 26%) and (iii) for formaldehyde, production of gas standards using certified permeation tubes (Eco-Scientific, UK), diluted, appropriately humidified and delivered to the CIR-TOF-MS sample inlet by a commercial calibration unit (Kintec, model: 491; calibration accuracy = 28%). Overall uncertainties for formaldehyde and cyclohexanone measurements made by CIR-TOF-MS were calculated to lie within the ranges 1.8-16.5 and 0.4-0.7 ppbV, respectively. CIR-TOF-MS measurement uncertainty values comprise the combination of both instrument precision and calibration accuracy,

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accounting for measurement reproducibility and known systematic uncertainty. The cyclohexyl-hydroperoxide observations, performed by HPLC, had an estimated uncertainty of 30%.

The radical measurements were performed by LIF (HO<sub>2</sub>) and PERCA ( $\Sigma$ HO<sub>2</sub> + RO<sub>2</sub>). The LIF system was calibrated before, during and after each measurement campaign using the H<sub>2</sub>O photolysis/ozone actinometry approach;<sup>44</sup> calibrations were constant to within a few percent. The estimated uncertainty in the LIF data from a single calibration is 27% (combined systematic error and precision)<sup>37,45</sup> although this may be regarded as conservative as the precision contribution from calibration will, to a certain extent, average out across the experiments. The instrument was calibrated as a function of humidity—in keeping with previous results (*e.g.* Creasey *et al.*)<sup>46</sup> a reduction in the instrument sensitivity is observed as humidity is initially increased from near-dry conditions, but the response flattens out within the range of humidities employed here.

The PERCA was calibrated using methyl iodide photolysis followed by subsequent methyl radical reaction with oxygen to generate methylperoxy radicals, thus determining the chain length of the chemical amplification.<sup>47</sup> An NO<sub>2</sub> permeation device was used to determine the sensitively of the Scintrex (Luminol chemiluminescence detector) to the NO<sub>2</sub> product of the amplification as per Fleming *et al.*<sup>48</sup> The accuracy of peroxy radical measurements with the Leicester dual channel PERCA is discussed in detail elsewhere.<sup>49</sup> The overall uncertainty of peroxy radical measurements is 38% (at  $2\sigma$ ) from a combination of uncertainties associated with the radical calibration, NO<sub>2</sub> quantification and humidity correction.

#### 2.4 Box model and mechanism optimisation

As  $HO_x$  radicals are highly reactive in the experimental system, results were interpreted through detailed chemical box modelling, drawing upon the ethene photochemical degradation scheme in the Master Chemical Mechanism (MCMv3.1);<sup>32,33,50</sup> in order to account for secondary chemical processes. The MCM is a near explicit chemical mechanism, describing the detailed gas-phase chemical processes involved in the atmospheric degradation of important primary emitted VOCs. The complete gas-phase photo-oxidation mechanism for ethene was extracted (including a suitable set of inorganic reactions) from the MCM and incorporated into a chamber specific box model. The MCM ethene photooxidation mechanism was updated to include a more explicit representation of the ethene-ozone reaction mechanism (Fig. 1) and chamber processes (dilution). Within the model, the rapid reaction steps occurring after formation of the primary ozonide (reactions 1b–4 in Fig. 1) were assumed to proceed near-instantaneously on the 1–2 hour timescale of the experiments; that is, reactions 1b, 2, 3a–c and 4 were not assigned individual rate constants—rather the POZ and [CH<sub>2</sub>OO]\* were assumed to decompose rapidly to form radical products (yields optimised as described below) and stable species, or the stabilised CH<sub>2</sub>OO, *via* reaction 4. Rate constants for the bimolecular reactions of the SCI (reactions 4a–c) were taken directly from the MCM. The MCMv3.1 cyclohexane photo-oxidation mechanism was also updated and extended, as outlined below. The chamber box model simulations were integrated using FACSIMILE.<sup>51</sup>

The initial conditions for each of the five experiments, as shown in Table 2, were used for the initialization of the corresponding box models. Temperature, relative humidity and dilution rates were averaged over the duration of each experiment, as the variation in these parameters was minimal. The simulations were initialized at the time point at which the maximum measured ethene mixing ratio was observed.

Four analytical stages were performed, in each case to determine the *overall* yields of specific products from the *overall* fast ozonolysis reaction (*i.e.* the CI formation/ decomposition chemistry), which are then interpreted in terms of branching ratios for each channel within the postulated mechanism.

**2.4.1 Reaction rate coefficient**  $(k_{O_3} + \text{ethene})$  **optimisation.** The recommended rate coefficient for ethene + ozone  $(k_{O_3} + \text{ethene})$  has an estimated uncertainty of 30%, <sup>1,24</sup> and the model representation of the measured ethene decay could be improved by optimising  $k_{O_3} + \text{ethene}$ , to simulate (fit) the observed ethene and ozone time profiles. This was achieved by using the FT-IR observations of ethene and ozone and by minimising the sum of squares of residuals between the measured and modelled results within FACSIMILE. Scavenger experiment types (b) and (c) were used to determine the rate coefficient, to suppress the OH + ethene reaction. Under these conditions, the loss of ethene can be considered to be due to dilution (known) and reaction with ozone only, allowing the reaction rate coefficient between ethene and ozone to be determined.

**2.4.2** SCI branching ratio calculation. In the simple ethene + ozone system, type (a) experiment, HCHO is formed *via* the decomposition of the POZ, the SCI + CO reaction 4b and the SCI +  $H_2O$  reaction 4c—see Fig. 1—and is also formed as a first- and multi-generation product of the OH + ethene reaction (*e.g.* from HOCH<sub>2</sub>CH<sub>2</sub>O decomposition). In addition the two loss pathways of HCHO in the simple, type (a) system were dilution and reaction with OH. In the

 Table 2
 Initial conditions for EUPHORE experiments

Expt. type	Ethene/ppbV	Ozone/ppbV	CO/ppmV	Cyclohexane/ppmV	Relative humidity/%	Dilution <sup><i>e</i></sup> /s <sup>-1</sup> (10 <sup>-5</sup> )	Temp/K	Duration/min
a	501.1	478.3	0.753	0	0.3	6.75	293.1	130
b	522.8	486.7	570	0	0.3	7.21	295.2	80
с	490.5	469.0	0.281	18.5	0.3	4.64	296.2	200
b	433.1	455.6	633	0	0.2	5.04	300.4	100
b+d	264.8	242.3	504	0	29.0	4.88	302.8	90
<sup>a</sup> Simple etl	hene and ozone	. <sup>b</sup> With added	CO. <sup>c</sup> With	added cyclohexane. d	With added water. <sup>e</sup> D	erived from decay of S	$SF_6$ , monito	ored by FT-IR.



**Fig. 2** Formaldehyde production as a function of ethene consumed for an excess CO experiment (Table 2). Data have been corrected for dilution, and determine an overall yield of HCHO with respect to ethene of 1.54.

excess CO experiments, the production of HCHO arises from the decomposition of the POZ (1b) and the SCI + CO reaction (4b), while the loss of HCHO is due to dilution only. It can be assumed from the postulated mechanism (Fig. 1) and previous studies,  $^{52,53}$  that the primary formaldehyde yield, formed directly from the decomposition of the POZ, is unity; correspondingly yields in excess of 1 are believed to reflect HCHO formation *via* reaction 4b, allowing the SCI branching ratio to be determined, assuming reaction with CO competes effectively with all other possible bimolecular fates of the SCI under the experimental conditions. The HCHO yield was obtained from regression of the HCHO production *vs.* C<sub>2</sub>H<sub>4</sub> consumption, following correction for dilution (Fig. 2).

2.4.3 OH yield optimisation. The steady-state OH concentrations generated in the ethene-ozone system were below the detection limit of the LIF system. OH yields were determined indirectly employing the excess cyclohexane system. The cyclohexane experiments were designed to scavenge  $\geq 95\%$  of any OH produced from ethene ozonolysis, generating products illustrated in Fig. 3a.<sup>43,54</sup> The cyclohexanone formed arises from OH reacting with cyclohexane (including both OH formed directly from the ozonolysis reaction, and that produced indirectly via  $HO_2 + O_3$ ). The ratio of cyclohexanone/ cyclohexyl-hydroperoxide formed and the fate of the cyclohexylperoxy radical, c-C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>, depend upon the concentrations of HO<sub>2</sub> and RO<sub>2</sub>, and identity of the RO<sub>2</sub>, present in the system, as these compete for reaction with  $c-C_6H_{11}O_2$ . Cyclohexanone "yields" from OH + cyclohexane are therefore not necessarily expected to be consistent between chemical systems, or indeed within the same chemical system at different (peroxy radical) concentration levels, with the key being the relative rates of the cyclohexylperoxy +  $RO_2$  and +HO<sub>2</sub> reactions. Using the cyclohexanone (as measured by CIR-TOF-MS), cyclohexyl-hydroperoxide (HPLC) and steady state HO<sub>2</sub> (LIF) observations, plus the ethene and O<sub>3</sub> data, the ratio  $k_6/k_7$  (where  $k_6 = k_{6a} + k_{6b} + k_{6c}$ ; see Fig. 3a) for the fate of the peroxy radical  $c-C_6H_{11}O_2$  and the OH yield can be obtained. This was achieved by minimising the sum of the square of the residuals between the simulations and



**Fig. 3** (a) Cyclohexane-OH oxidation scheme (adapted from the MCMv3.1 and ref. 57–59). (b) Schematic representation of the major decomposition (ring-opening) pathways of the cyclohexoxy radical chemistry under zero  $NO_x$  conditions. See Table S1 (ESI†) for a full list of the cyclohexoxy reactions used in the simulations.

observations for cyclohexanone, cyclohexyl-hydroperoxide and HO<sub>2</sub> data whilst optimising the ratio  $k_6/k_7$  and OH yield and constraining C<sub>2</sub>H<sub>4</sub> and O<sub>3</sub> to their observed levels. The MCMv3.1 cyclohexane mechanism was updated to include a more explicit representation of the OH-initiated ring opening chemistry, accounting for the decomposition/isomerisation reactions of the cyclohexoxy radical as shown in Fig. 3a and b. The atmospheric chemistry of the cyclohexoxy radical involves competition between unimolecular decomposition *via* ring-opening (8b) and reaction with O<sub>2</sub> (8a)—unimolecular isomerisation (8c) is found to be negligible owing to ring strain (Fig. 3a).<sup>55,56</sup> The rate coefficients for the cyclohexoxy radical + O<sub>2</sub> reaction, 8a, and the unimolecular decomposition of the cyclohexoxy radical, 8b, used in this study were 2.5 ×  $10^{-14} \exp^{(-300/T)}$ ,<sup>57</sup> and  $3.8 \times 10^{-13} \exp^{(-6026/T)}$ ,<sup>58</sup> respectively, which correspond to a yield of 0.43 for cyclohexanone from reaction 8a under atmospheric conditions. This is found to be in reasonable agreement with Orlando *et al.* (2000):<sup>59</sup> 0.36 ± 0.06, and good agreement with Welz *et al.*<sup>58</sup> (0.43), Atkinson *et al.*<sup>43</sup> (0.42 ± 0.05), and with the average yield of 0.41 ± 0.08 derived from literature studies, <sup>58–62</sup> calculated using the Atkinson (2007)<sup>57</sup> recommended rate coefficient for secondary peroxy radical reactions with O<sub>2</sub> in all cases, as above.

2.4.4 HO<sub>2</sub> optimisation. The HO<sub>2</sub> yield was determined by using FT-IR measurements for ethene and ozone and LIF observations for HO<sub>2</sub> and minimising the sum of the square of the residuals between the simulated and observed concentrations. Fig. 1 illustrates that the formation of OH is likely to be accompanied by a formyl radical from reactions 2 and 3a, which under the experimental conditions would react rapidly with  $O_2$  forming  $HO_2$  + CO. The sum of channels 2 and 3a therefore gives the overall  $Y_{OH}$  and also accounts for a fraction of the HO<sub>2</sub> yield; as the overall  $Y_{OH}$  is calculated during stage 3, channels 2 and 3a can be combined and quantified within the model. In this representation of the reaction mechanism, the remaining channel producing  $HO_2$  in the ethene-ozone system to be quantified is 3b, where 2 H atoms react near-instantaneously with O2 to form 2 HO2. Channel 3b was optimised within the model to best reproduce the observed HO<sub>2</sub> concentrations. The sum of the combined branching ratios 2 + 3a (determined in stage 3—OH yield optimisation) and 3b, determine the overall yield of HO<sub>2</sub>.

#### 3. Results

The ethene + ozone reaction rate coefficients,  $k_{O_3}$ +ethene, determined from the scavenger experiments (Table 2) were

1.33, 1.37 and 1.55 (×10<sup>-18</sup>) cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 295.2 K, 296.2 K and 300.4 K respectively. This corresponds to a value of  $(1.45 \pm 0.25) \times 10^{-18}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298 K which was subsequently used for all simulations performed. The indicated uncertainty is combined precision (1 $\sigma$ ) and systematic uncertainty of the instrumentation, see Section 2.3. This value is in good agreement with previous studies (see Table 3), and is approximately 10% lower than the IUPAC recommendation,<sup>24</sup> which has an estimated uncertainty of ±30%. The rate constant for ethene ozonolysis is relatively slow in comparison to other small chain alkenes, such that the primary loss of ethene in the chamber is from dilution rather than chemical loss.

The mean total HCHO yield (i.e. production via both pathways 1b and 4b) calculated from the excess CO experiments (Table 2) was  $1.54 \pm 0.12$ , corresponding to a branching ratio for the SCI  $(Y_{SCI})$  of 0.54. The reported uncertainty is the combined precision  $(1\sigma)$  and systematic uncertainty of the instrumentation, see Section 2.3. The HCHO yield was obtained from regression of the HCHO concentration as a function of the change in ethene concentration, after correction for dilution (Fig. 2). The value is at the upper end of the previous reported literature range (Table 3). Fig. 4 shows a comparison between the observed and modelled C2H4, O3 and HCHO mixing ratios after optimisation of the ethene + ozone rate constant, and before/after optimisation of the SCI yield. Increasing the SCI yield from 0.37 (as specified in MCMv3.1) to 0.54 (this study) markedly improves agreement between the HCHO observations and the simulation, to within 3%.

An overall OH yield ( $Y_{\rm OH}$ ) for ethene ozonolysis in the presence of cyclohexane (OH scavenger experiment type (c), see Table 2) of  $0.17 \pm 0.09$  was obtained (shown in Table 4), attributed to the combined branching ratios (2) + (3a). The OH yield was determined by fitting the cyclohexanone, cyclohexyl-hydroperoxide and HO<sub>2</sub> observations, as described in Section 2.4 and shown in Fig. 5. The fit to the OH-initiated

Table 3 Comparison of reaction rate coefficient ( $k_{O_3+ethene}$ ) and yield of stabilised Criegee intermediate CH<sub>2</sub>OO from this work and previous studies

Rate constant/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> at 298 K (×10 <sup>-18</sup> )	Yield of SCI $(Y_{SCI})$	SCI scavenger type	Reference
$\frac{(1.45 \pm 0.25)^{a}}{(1.59 \pm 0.30)}$ $\frac{(1.45 \pm 0.10)}{(1.37 \pm 0.08)}$ $\frac{(1.59 \pm 0.30)}{1.44^{b}}$	$\begin{array}{c} 0.54 \pm 0.12^{a} \\ 0.37 \\ 0.40 \\ 0.35 \pm 0.05 \\ 0.37 \pm 0.02 \\ 0.38 \\ 0.39 \pm 0.11 \end{array}$	CO HCHO HCHO HCHO HCHO H2O and HCOOH	This study MCMv3.1 (IUPAC) <sup>24</sup> Bahta <i>et al.</i> <sup>89</sup> Treacy <i>et al.</i> <sup>90</sup> Atkinson and Arey <sup>91</sup> <sup>c</sup> Qi <i>et al.</i> <sup>28</sup> This study MCMv3.1 (IUPAC) <sup>24</sup> Atkinson and Lloyd <sup>85</sup> Niki <i>et al.</i> <sup>67</sup> Kan <i>et al.</i> <sup>81</sup> Su <i>et al.</i> <sup>66</sup> Hasson <i>et al.</i> <sup>92</sup>
	$\begin{array}{c} 0.39 \pm 0.053 \\ 0.47 \pm 0.05 \\ 0.50 \pm 0.04 \\ 0.51 \\ 0.52 \end{array}$	$SO_2$ Total yield of decomposition products HCOOH Total yield of decomposition products CF <sub>3</sub> C(O)CF <sub>3</sub>	Hatakeyama <i>et al.</i> <sup>65</sup> Horie and Moortgat <sup>87</sup> Neeb <i>et al.</i> <sup>70</sup> Neeb <i>et al.</i> <sup>69</sup> Horie <i>et al.</i> <sup>93</sup>

<sup>*a*</sup> The error of  $k_{O_3+\text{ethene}}$  and  $Y_{\text{SCI}}$  was determined from the uncertainty of the instrumentation and the standard deviation (1 $\sigma$ ) of repeated experiments. <sup>*b*</sup> Error not specified. <sup>*c*</sup> Also recommendation of ref. 1.



**Fig. 4** FT-IR Observed temporal profiles of  $C_2H_4$  (circles),  $O_3$  (squares) and HCHO (triangles) plus model simulations (solid lines) for an excess CO scavenger experiment type (b) (see Table 2). Model simulations for optimised  $k_{O_3+\text{ethene}}$  with SCI branching ratio of 0.54 (solid line) and 0.37 (current IUPAC recommended value) (dashed line) – see text.

cyclohexane oxidation products (c-C<sub>6</sub>H<sub>10</sub>O and c-C<sub>6</sub>H<sub>11</sub>OOH), HO<sub>2</sub>, ethene and ozone gave a  $k_6/k_7$  ratio of 0.44, which corresponds to the lower limit ( $ca. 5.0 \times 10^{-12}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>) of literature values for  $k_7$  of  $1.70 \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>.<sup>63,64</sup> The MCMv3.1 RO<sub>2</sub> permutation rate coefficient (for >C<sub>3</sub> alkyl) of 2.5 ×  $10^{-12}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> was used for  $k_6$  overall,<sup>33</sup> while the branching ratios for reactions 6a, 6b and 6c used in the simulations were 0.6, 0.2 and 0.2 respectively, in good agreement with Rowley *et al.*<sup>61</sup> who determined ratios of 0.58 and 0.42 for 6a and (6b + 6c) respectively.

The HO<sub>2</sub> yields  $(Y_{HO_2})$  obtained for the four types of experiments are shown in Table 5. The apparent decrease in  $Y_{HO_2}$  in the presence of excess CO (experiment type b) is discussed in Section 4. For the direct system (C<sub>2</sub>H<sub>4</sub>/O<sub>3</sub>) an HO<sub>2</sub> yield of 0.30 ± 0.08 was determined; where the indicated uncertainty arises from the uncertainty in the LIF system measurement (see Section 2.3). The value of  $Y_{HO_2}$  obtained is in reasonable agreement with the limited previous literature (Table 5). Using the mean  $Y_{HO_2}$  from both the simple and cyclohexane experiments, 0.27 ± 0.07, the product branching

**Table 4** Comparison of OH formation yields from this work andprevious studies

Yield of OH	Method	Reference
$0.17 \pm 0.09^{a}$	This Study	This study
0.16	IUPAC	http://www.iupac-kinetic.
		ch.cam.ac.uk/
0.13	MCMv3.1	http://mcm.leeds.ac.uk/MCM
$0.18\pm0.06$	Tracer	Paulson <i>et al.</i> <sup>18</sup>
$0.14\pm0.07$	Tracer	Rickard et al. <sup>19</sup>
$0.20\pm0.02$	MI-ESR	Mihelcic et al. <sup>27</sup>
$0.12\pm0.06$	Cyclohexane	Atkinson et al.43
ca. 0.14	Low pressure LIF	Kroll <i>et al.</i> <sup>23</sup>
$0.00\pm0.05$	Stoichiometry	Wegener et al. <sup>30</sup>
$\leq 0.05$	Calculation	Gutbrod et al.25
$0.08\pm0.01$	CO	Gutbrod <i>et al.</i> <sup>21</sup>
$0.22\pm0.06$	Tracer	Fenske et al. <sup>77</sup>

<sup>*a*</sup> The uncertainty in  $Y_{OH}$  represents combined instrumental factors (51%) and uncertainty associated with the branching ratio for decomposition of cyclohexoxy radical.



Fig. 5 Observed temporal profiles of cyclohexanone (c-C<sub>6</sub>H<sub>10</sub>O—open squares, from CIR-TOF-MS), cyclohexyl-hydroperoxide (c-C<sub>6</sub>H<sub>11</sub>OOH—grey triangles, from HPLC) and steady state [HO<sub>2</sub>] (black circles, from LIF) plus optimised model simulations (lines); data determine the OH yield.

ratios (2), (3a) and (3b) for the mechanism illustrated in Fig. 1 can be assigned. The  $Y_{OH}$  of 0.17 also corresponds to the total yield of HCO formed alongside OH; this HCO reacts near instantaneously with O<sub>2</sub> to form HO<sub>2</sub>. The remaining branching ratio, channel 3b forming 2 HO<sub>2</sub>, is therefore 0.05.

The observed decrease in  $Y_{\rm HO_2}$  when increasing the relative humidity from 0.2 to 29.0% is illustrated in Fig. 6. A slightly larger decrease was seen in the observed HO<sub>2</sub> +  $\Sigma RO_2$ measurements made by the PERCA instrument in comparison to the LIF measurements for HO<sub>2</sub>, when increasing the humidity. RO2 concentrations (which would presumably be  $HOCH_2CH_2O_2$ , formed from OH + ethene) are expected to be minimal in this system, and so the discrepancies between the two independent methods are likely owing to instrumental uncertainties or artefact(s) (as discussed in Section 2.3). The LIF measurements are well simulated for the first  $\sim$ 95 minutes of the experiment, with an overall optimised yield of 0.10 for HO<sub>2</sub>, but the model could not reproduce the observed decrease in HO<sub>2</sub> seen after increasing the humidity. The decrease in the simulated HO<sub>2</sub> observed with increasing [H<sub>2</sub>O] arises from the humidity dependence of the HO2 self reaction, as no H2O dependence was applied to the HO<sub>2</sub> yield in the model

 Table 5
 HO2 yields derived vs. experimental conditions

Scavenger/method	Yield of HO <sub>2</sub>	Reference
Simple $C_2H_4 + O_3$ Excess CO (expt., 1) Excess CO (expt., 2) Excess cyclohexane Excess CO + H <sub>2</sub> O	$\begin{array}{c} 0.30 \pm 0.08 \\ 0.10 \pm 0.03 \\ 0.10 \pm 0.03 \\ 0.24 \pm 0.12^{a} \\ 0.05 \pm 0.01 \end{array}$	This study This study This study This study This study This study
Average (simple + excess cyclohexane)	$0.27\pm0.07$	This study
MCMv3.1 MI-ESR PERCA Stoichiometry (dry) Stoichiometry (wet)	$\begin{array}{c} 0.13 \\ 0.39 \pm 0.03 \\ 0.38 \pm 0.02 \\ 0.50 \pm 0.25 \\ 0.40 \pm 0.20 \end{array}$	http://mcm.leeds.ac.uk/MCM Mihelcic <i>et al.</i> <sup>27</sup> Qi <i>et al.</i> <sup>28</sup> Wegener <i>et al.</i> <sup>30</sup> Wegener <i>et al.</i> <sup>30</sup>

<sup>*a*</sup> The uncertainty in  $Y_{\rm HO_2}$  represents combined uncertainty from the instrumentation used and uncertainty associated with the branching ratio for decomposition of cyclohexoxy radical.



**Fig. 6** Temporal profile of HO<sub>2</sub> (LIF, grey circles) and HO<sub>2</sub> +  $\Sigma$ RO<sub>2</sub> (PERCA, black triangles) plus model simulations before (dashed line, base case MCMv3.1 chemistry) and after (solid line) optimising the HO<sub>2</sub> yield to the LIF data, for an excess CO scavenger experiment (type (b), see Table 2). H<sub>2</sub>O was added to increase the humidity from 0.2% to 29% RH over a 26 minute period from 97 min (dotted lines). Modelled variation in HO<sub>2</sub> with increased RH reflects secondary chemical effects (HO<sub>2</sub> self-reaction) only.

mechanism. The humidity dependence of the HO<sub>2</sub> + HO<sub>2</sub> reaction is well defined<sup>24</sup> with an uncertainty of approximately 30%; the reaction rate constant would have to be in error by a factor of 2 to account for the observed trend in isolation, suggesting that  $Y_{\rm HO_2}$  in the ethene ozonolysis reaction decreases with increased humidity, under the conditions of these experiments (*i.e.* in the presence of excess CO).

#### 4. Discussion

The SCI yield ( $Y_{SCI}$ ) obtained of 0.54  $\pm$  0.12 is slightly larger than that reported by Hatakeyama et al.,<sup>65</sup> (0.39  $\pm$  0.05), who measured the yield of sulphuric acid  $(H_2SO_4)$  formed from the ozonolysis of ethene in the presence of SO<sub>2</sub>. In this study it was assumed that the SCI was scavenged by reaction with SO<sub>2</sub>, forming SO<sub>3</sub>, which was further converted to H<sub>2</sub>SO<sub>4</sub> aerosol. The yields determined by Su *et al.*<sup>66</sup> and Niki *et al.*<sup>67</sup> are also lower than that obtained in this study (Table 3). These studies used long path FT-IR spectroscopy to measure the yield of what was thought to be hydroxy methyl formate (HMF, HOCH<sub>2</sub>OCHO) as a product from the reaction of  $CH_2OO +$ HCHO. However, this product was later identified as being hydroperoxy methyl formate (HPMF, HOOCH<sub>2</sub>OC(O)H).<sup>68</sup> The  $Y_{SCI}$  value obtained here is, however, in good agreement with the studies of Neeb and co-workers<sup>69,70</sup> who report a HPMF yield of 0.51 in the presence of excess HCOOH (exploiting the reaction SCI + HCOOH),<sup>70</sup> and deduce the total yield of decomposition products from the excited CI, respectively.<sup>69</sup> The  $Y_{SCI}$  has also been found to be pressure dependent, where it is reported that a significant fraction  $(0.20 \pm 0.03)$  of the initial [CH<sub>2</sub>OO]\* formed is thermally "cold" at low pressure,<sup>71</sup> determined from extrapolation of measurements over the range 13 mbar to 1.5 bar.

The calculated  $Y_{\rm OH}$  of 0.17  $\pm$  0.09 is consistent with the recent literature (Table 4). Paulson *et al.*<sup>18</sup> and Rickard *et al.*<sup>19</sup> employed OH radical tracer methods to obtain yields of

 $0.18 \pm 0.06$  and  $0.14 \pm 0.07$  respectively, both in good agreement with this study. Gutbrod et al.<sup>21</sup> use excess CO as an OH scavenger, reporting a  $Y_{OH}$  of  $0.08 \pm 0.01$  by detecting CO2 as a product of the CO + OH reaction. Ab initio calculations made prior to their study, however, estimate a  $Y_{\text{OH}}$  of  $\leq 0.05$ .<sup>25</sup> Atkinson and co workers<sup>43</sup> measured an OH yield of 0.12 from ethene ozonolysis using cyclohexane as an OH scavenger, which is also found to be in reasonable agreement with this work, but has a reported uncertainty of a factor of 1.5 (*i.e.*  $\pm 0.06$ ) owing to the unknown HO<sub>2</sub> concentration in the system, and therefore uncertain contribution of the  $HO_2 + O_3$  reaction to the total OH. Previous studies using cyclohexane as an OH scavenger have monitored the production of cyclohexanone + cyclohexanol (or just cyclohexanone itself) relative to the extent of alkene ozonolysis in order to determine an OH yield, based upon a known (or measured) yield of cyclohexanone (+cyclohexanol) from the OH-initiated oxidation of cyclohexane. The yield of OH is then determined from eqn (9):

$$Y_{\rm OH} = \frac{[\text{cyclohexanone}](+[\text{cyclohexanol}])/\Delta[\text{alkene}]}{[\text{cyclohexanone}](+[\text{cyclohexanol}])/\Delta[\text{cyclohexane}]}$$
(9)

There have been numerous studies calculating the yield of cyclohexanone + cyclohexanol from the OH-initiated oxidation of cyclohexane, giving a range of values between 0.50-0.88.43,61,72,73 More recently,  $Y_{OH}$  has been determined by monitoring the evolution of the parent alkene relative to the production of cyclohexanone only.<sup>54,73,74</sup> A range of yields of cyclohexanone from the OH-initiated oxidation of cyclohexane have also been reported: 0.26–0.53.<sup>1,43,54,61,73</sup> However, a study of the mechanism of the self reaction of CH3OCH2O2, analogous to c-C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>, suggests that the yield of cyclohexanone from the OH-initiated oxidation of cyclohexane should always be close to 0.5.75 The range in the reported yields is likely to arise from the varying flux through the HO<sub>2</sub> reaction (reaction 7 in Fig. 3a) between studies, as the yield of cyclohexyl-hydroperoxide is dependent on the HO<sub>2</sub> concentration, in competition with reactions 6a, 6b and 6c. This, coupled with the decomposition/isomerisation reactions of the cyclohexoxy radical (reactions 8b and 8c in Fig. 3), results in a less than unity yield of cyclohexanone and cyclohexanol. The yields observed will depend upon the relative concentrations of RO<sub>2</sub> and HO<sub>2</sub> radicals (and RO<sub>2</sub> speciation) present, and will therefore be dependent on the specific reaction system and reagent concentrations used. Thus, this scavenger technique may result in a large variation in  $Y_{OH}$  if applied to systems where the HO<sub>2</sub> and/or RO<sub>2</sub> present differ from those under which the cyclohexanone/cyclohexanol yields from cyclohexane were originally determined.

In this work, owing to the slow ethene  $+ O_3$  rate coefficient and the low OH yield, approximately 40% of the OH formed in the overall ethene + ozone system comes from reaction (10):

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{10}$$

If  $Y_{OH}$  were calculated using eqn (9) (*i.e.*, from the relationship between the cyclohexanone formed *versus* the amount of

ethene reacted), while adopting an average cyclohexanone yield of 0.528 from recent cyclohexane + OH oxidation studies;<sup>54,73</sup> an overall OH yield of 0.09  $\pm$  0.02 would be obtained. Allowing for the OH formation from  $HO_2 + O_3$ , an effective  $Y_{OH}$  of 0.05 for the direct decomposition of [CH<sub>2</sub>OO]\* would be obtained, a factor of 3 smaller than the value determined through the model optimisation approach. This highlights the importance of considering the detailed scavenger chemistry as well as the concentration of HO<sub>2</sub> under high [O<sub>3</sub>]/[ethene] conditions. Mihelcic et al.,<sup>27</sup> determined a  $Y_{\rm OH}$  of 0.20  $\pm$  0.02, by measuring HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> using the MIESR technique, as this peroxy radical is a direct product of the  $C_2H_4$  + OH reaction. This slightly larger  $Y_{OH}$  may reflect secondary OH formation from  $HO_2 + O_3$ ; for the present work, if the secondary OH formation via reaction (10) is combined with the 0.17 OH yield determined for the direct isomerisation/decomposition of [CH2OO]\*, (calculated by OH vield optimisation simulations, in which the  $HO_2 + O_3$ reaction is accounted for), an OH formation (primary and secondary) yield of 0.24 would be obtained.

The first direct evidence for OH formation in the ethene ozonolysis system was obtained by Donahue et al.22 from LIF observations at a total pressure of 5 Torr, with a reported  $Y_{OH}$ of  $0.43 \pm 0.20$ . Subsequent studies from the same laboratory confirmed that the OH radical formation was not pressure dependent,  $^{23,76}$  and reported a refined Y<sub>OH</sub> of 0.14, corresponding to prompt OH production over short timescales  $(\sim 30 \text{ ms})$  at pressures between 10–60 Torr.<sup>23</sup> This suggests that OH is not formed by the direct dissociation of the excited CI [CH<sub>2</sub>OO]\*, but rather via fragmentation of a 'hot' formic acid intermediate, as shown in reaction 3a in Fig. 1. In contrast, however, the pressure dependence of OH yields was also investigated by Fenske et al.,77 who reported an increase in OH formation with decreasing pressure from  $0.22 \pm 0.06$  at 760 Torr to  $0.61 \pm 0.18$  at 20 Torr. The authors proposed an alternative biradical pathway at low pressures, but could not preclude that the 'hot' formic acid formed from the dioxirane could serve as a pressure dependent source of OH. Kroll et al.<sup>76</sup> attributed this increase in OH production at low pressures to bimolecular reactions of reactive intermediates, which could be significant over longer timescales. To date, direct measurements of OH from ethene ozonolysis at atmospheric pressure using LIF have not been achieved; thus, although there is strong evidence that OH is formed from the fragmentation of 'hot' formic acid at lower pressures (10-60 Torr) and short time scales (on the order of ms) the lack of direct measurements at atmospheric pressure, both at short and long timescales, means that OH formation from the direct dissociation of the excited CI [CH2OO]\* cannot be ruled out. Fig. 1 illustrates that the production of OH may result from both channels 2 and 3a; the data obtained here cannot distinguish between these routes and so channels 2 and 3a are summed, giving an overall OH yield.

The HO<sub>2</sub> yields  $(Y_{HO_2})$  calculated for the different types of experiments are shown in Table 5, where the values obtained, together with the previous literature, suggest that the yield of HO<sub>2</sub> currently used in the MCMv3.1 (0.13) is an underestimate. Wegener *et al.*<sup>30</sup> exploited reaction 10 to evaluate HO<sub>2</sub> formation from the additional ozone turnover (over and above

that due to reaction with ethene) in excess CO experiments, deriving an HO<sub>2</sub> yield,  $Y_{\rm HO_2}$  of 0.50  $\pm$  0.25. The large uncertainty reflects the small contribution of the  $HO_2 + O_3$ reaction to the total consumption of O<sub>3</sub>, but is in agreement (within uncertainty) with this work. The PERCA  $HO_2$  +  $\Sigma RO_2$  data obtained here are consistent (within uncertainty) with the HO<sub>2</sub> observations for the ethene/ozone/CO system (Fig. 6), and indicate that organic peroxy radical levels in this system are small. This is in accord with our understanding of the mechanism (Fig. 1), and the presence of an OH scavenger (CO). The PERCA data also (independently) display the same trend with added water vapour as the LIF HO<sub>2</sub> observations, over and above that anticipated from the humidity dependence of the HO<sub>2</sub> self-reaction, as discussed further below. The decrease in  $Y_{HO_2}$  seen when increasing relative humidity from 0.2 to 29.0% is in qualitative agreement with Wegener et al.,<sup>30</sup> who report decreases, albeit with large uncertainty, in  $Y_{\rm HO_2}$  with enhanced humidity for the ozonolysis of ethene  $(0.50 \pm 0.25$  to  $0.40 \pm 0.20)$ , propene  $(1.50 \pm 0.75$  to  $1.15 \pm 0.60)$  and isobutene  $(2.00 \pm 1.00$  to  $1.60 \pm 0.08$ ).

Mihelcic *et al.*<sup>27</sup> measured  $Y_{HO_2}$  by MIESR in the presence and absence of CO, and found that the overall  $Y_{HO_2}$  increased from 0.39 to 0.66 in the presence of excess CO (arising from the total HO<sub>x</sub> radical yield, OH + HO<sub>2</sub>). The observed increase in  $Y_{HO_2}$  in the presence of CO is in contrast to this work, where a decrease in  $Y_{HO_2}$  was seen (after accounting for additional HO<sub>2</sub> production *via* OH + CO). Mihelcic *et al.*,<sup>27</sup> however, used large initial concentrations of ethene (*ca.* 125–350 ppmV) to ensure that the ozonolysis kinetics were pseudo-first-order with respect to O<sub>3</sub>, and used a reaction rate coefficient,  $k_{O_3+ethene}$ , which is 40% smaller than the currently accepted value for their analysis, stating that the use of a larger value (such as current evaluations recommend) for  $k_{O_3+ethene}$ would result in the radical yields decreasing by ~40%.

The apparent decrease in  $Y_{\rm HO_2}$  observed in the presence of excess CO is not consistent with the mechanism presented in Fig. 1, which suggests that the  $Y_{\rm HO_2}$  would remain the same while the observed [HO2] increases due to the formation of  $HO_2$  via the reaction of OH + CO. In order to account for this behaviour, we consider three possible explanations: Firstly, bimolecular reactions with a partially stabilised CI. There are three potential channels that form HO<sub>2</sub>; direct decomposition of the CI to form OH + HCO (HCO +  $O_2 \rightarrow HO_2 + CO_2$ ) (reaction (2) in Fig. 1), and two branching ratio products from the fragmentation of 'hot' formic acid forming OH + HCO (reaction 3a) and CO<sub>2</sub> + 2H (H + O<sub>2</sub> + M  $\rightarrow$  HO<sub>2</sub> + M) (reaction 3b). It has been shown that OH formation from alkene ozonolysis can result from both prompt formation from a vibrationally excited CI and formation from the decomposition of a partially "thermalised" CI, at longer timescales.<sup>7,76</sup> Thus, there is the possibility for bimolecular reactions to occur with the partially thermalised CI interrupting the decomposition process, particularly in the presence of excess CO, as illustrated in Fig. 7. This could also account for the sub-unity OH yield observed for the substituted alkene species 2,3-dimethyl-2-butene,<sup>24</sup> where the hydroperoxide channel should be dominant with an expected OH yield of 1, but for which many studies measure a yield of < 1, giving rise

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to a recommended yield of 0.88.<sup>24</sup> This hypothesis has not (to our knowledge) been tested for the CH2OO CI and/or with CO as the scavenger, but was partially tested for the ozonolysis of 2-methyl-2-butene in the presence of the Criegee scavengers H<sub>2</sub>O, SO<sub>2</sub>, butanone and acetic acid.<sup>78</sup> The authors concluded that bimolecular reactions with the studied scavengers were too slow to inhibit OH formation. The proposed bimolecular reaction of CO with the partially stabilised CI would, however, only account for half of the overall observed HO<sub>2</sub> reduction in the CO scavenger experiments, if it is assumed that as an upper limit 100% of the OH formation from ethene ozonolysis at atmospheric pressure comes from the direct decomposition of [CH2OO]\* and not from the 'hot' formic acid. Scavenging of the partially stabilised CI would also contribute to the observed HCHO yield, as a product of the CO + SCI reaction, altering the overall SCI yield inferred.

A second possible explanation for the observed decrease in  $Y_{\rm HO_2}$  in the presence of excess CO is reaction of the dioxirane with CO resulting in the formation of formic anhydride (FAN).<sup>79,80</sup> In a previous study, Kuhne et al.<sup>79</sup> proposed a mechanism for the formation of FAN, shown in Fig. 8, and reported an increase in its yield in the presence of excess CO. This channel would compete with the isomerisation of the dioxirane to the 'hot' formic acid, should the lifetime of the dioxirane be sufficient. Kan et al.81 attributed the formation of FAN to the decomposition of hydroxyl methyl formate (HMF, HOCH<sub>2</sub>OCHO), a product of the reaction of SCI + HCHO, where Su *et al.*<sup>66</sup> had previously reported a FAN yield of 0.24 in the presence of excess CO, using FT-IR. However, more recently the infra-red spectrum attributed to HMF was reassigned to hydroperoxy methyl formate (HPMF, HOOCH<sub>2</sub>OCHO),<sup>68</sup> a product of the reaction of SCI + HCOOH, and a combined yield of 0.18 was assigned for both HPMF and FAN.<sup>69</sup> Relatively high levels of 2-9 ppmV of ethene and ozone, and either 5-50 ppmV of HCHO or 1–10 ppmV of HCOOH were used in these studies, in order to scavenge the SCI; Wolff *et al.*<sup>82</sup> confirmed the formation of HPMF in the ozonolysis of ethene in the presence of excess HCOOH, but also observed HPMF in the absence of HCOOH when using very large ethene concentrations. Under the conditions of our experiments, FAN would not be expected to arise from the decomposition of HPMF formed from SCI + HCOOH, as the SCI would be expected to react with the excess CO present, rather than HCOOH and/or HCHO.

Thirdly, the similar  $Y_{\rm HO_2}$  obtained for ethene–ozone experiments and those in which cyclohexane was present may indicate that the presence of SCI scavengers could be responsible for the decrease in  $Y_{\rm HO_2}$ . This could imply the occurrence of an independent HO<sub>2</sub> channel from the SCI, which may be inhibited in the presence of CO and/or H<sub>2</sub>O. Such a radical pathway has been proposed in a theoretical study investigating the unimolecular decomposition channels of hydroxymethyl hydroperoxide (HOCH<sub>2</sub>OOH or HMHP), the product of the CH<sub>2</sub>OO + H<sub>2</sub>O reaction.<sup>83</sup> The authors, however, also state that the water assisted decomposition of HMHP would yield further radical products, which is in contrast to the results of this study.

The branching ratio obtained for channel 3b of 0.05 (Fig. 1) equates to a H atom yield of 0.10, which is in agreement with the previously reported low pressure H atom yield of  $0.076 \pm 0.060$ .<sup>31</sup> This suggests that H atoms are formed *via* the hot acid channel, 3b, and not *via* the formyl radical, in agreement with *ab initio* calculations on the mechanism of HCO + O<sub>2</sub>.<sup>84</sup> A range of branching ratio determinations for channel 3b have been reported: 0.06-0.10;<sup>1.34,85–88</sup> all of which are in agreement, within uncertainty, with this study. Horie and Moortgat<sup>87</sup> derived a branching ratio of 0.09 for channel 3b by determining the H-atom yield from the increase in CO after addition of HCHO to the reaction system. Subsequently



Fig. 7 Possible routes to OH formation from the vibrationally excited CI.



Fig. 8 Proposed mechanism for the formation of formic anhydride (FAN) (after Kuhne et al.).<sup>79</sup>

Table 6 Branching ratios derived for the  $CH_2OO^*$  CI formed in the ozonolysis of ethene

Reaction number (see Fig. 1)	Reaction	Branching ratio
(2) + (3a)	$CH_2OO^* \rightarrow OH + HCO$	0.17
(3b)	$CH_{2}OO^* \rightarrow CO_2 + 2 H$	0.05
(3c)	$CH_{2}OO^* \rightarrow CO^+ H_{2}O$	$0.24^{a}$
(3d)	$CH_2OO^* \rightarrow CO_2 + H_2$	
(4)	$CH_2OO^* \rightarrow CH_2OO$	0.54
<sup>a</sup> Combined branch	ing ratio for reactions (3c) and (3d).	

Neeb *et al.*<sup>69</sup> showed that CO is also produced in the reaction of SCI + HCHO, and assigned a branching ratio of 0.23 to the combined channels 3b and 3d. Thomas *et al.*<sup>88</sup> studied the pressure dependence of the products of ethene ozonolysis, using long path FT-IR and GC/UV, determining branching ratios for channels 3b, 3c and 3d of 0.09, 0.31 and 0.13, respectively. With the quantification of the branching ratios determined during this study (0.17 for the combined branching ratios 2 and 3a, 0.05 for 3b and 0.54 for 4) the remaining branching ratios (3c and 3d) are combined to 0.24. The branching ratios derived for reactions 1–4 are summarised in Table 6.

#### 5. Conclusion

The reaction between ethene and ozone has been investigated in detail under ambient tropospheric boundary layer conditions using a range of instrumentation, including FT-IR, CIR-TOF-MS, PERCA and LIF. Ethene ozonolysis experiments in the presence and absence of cyclohexane and CO were performed with the results interpreted through detailed chemical box modelling. A reaction rate coefficient for ethene + ozone  $(k_{O_3+ethene})$  of  $(1.45 \pm 0.25) \times 10^{-18}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298 K was calculated by optimising  $k_{O_3+ethene}$  to best simulate the observed ethene and ozone decay traces. The postulated mechanism and previous studies indicate that the primary HCHO yield is unity; therefore, the averaged measured HCHO yield of  $1.54 \pm 0.12$  in the presence of excess CO is assumed to reflect the reaction of CH<sub>2</sub>OO with CO (leading to CO<sub>2</sub> and HCHO), determining an SCI yield of  $0.54 \pm 0.12$ .

An OH yield of  $0.17 \pm 0.09$  was derived from the isomerisation/decomposition of CH<sub>2</sub>OO\* (combined branching ratio of channels 2 + 3a, see Fig. 1), through numerical optimisation to observed concentrations of C<sub>6</sub>H<sub>11</sub>OOH, cyclohexanone, ethene, ozone and HO<sub>2</sub>. The results highlight the importance of accounting for the HO<sub>2</sub> abundance, particularly under relatively high O<sub>3</sub>/alkene conditions, and the detailed scavenger chemistry (to allow for RO<sub>2</sub> + HO<sub>2</sub> coupling and the O<sub>3</sub> + HO<sub>2</sub> contribution to the overall OH yield) when deriving radical yields in scavenger experiments.

A mean HO<sub>2</sub> yield of 0.27  $\pm$  0.07 was determined in the presence (0.24  $\pm$  0.12) and absence (0.30  $\pm$  0.08) of cyclohexane, with an apparent decrease in HO<sub>2</sub> yield observed in the presence of both CO (to 0.10  $\pm$  0.03) and increased humidity (to  $0.05 \pm 0.01$ ). Potential explanations for these dependencies are: (i) bimolecular reaction of the partially thermalised Criegee intermediate (CI) interrupting the decomposition process, particularly in the presence of CO scavenger; (ii) the reaction of CO + dioxirane, leading to the formation of formic anhydride (FAN); (iii) an additional HO<sub>2</sub> production channel from bimolecular reactions of the SCI, which competes with CO and H<sub>2</sub>O. These results are consistent with competition between radical production and bimolecular removal of the CH2OO carbonyl oxide, indicating that the "real" HO<sub>2</sub> yield from ethene ozonolysis under atmospheric conditions (with higher humidity and in the presence of other known CI co-reactants such as CO, SO<sub>2</sub> and NO) may be lower than is observed in simple ethene + ozone experimental systems.

From our results and previous studies, we suggest the following rate constant/yields are incorporated into atmospheric chemistry and air quality models where chemical detail is required:

 $O_3$  + ethene  $\rightarrow 0.17 \text{ OH} + 0.27 \text{ HO}_2 + 0.54 \text{ SCI} + 1.00 \text{ HCHO}$ 

 $k_{\text{O}_3 + \text{ethene}} = 1.45 \ (\pm 0.25) \times 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$ 

Data from alternative experimental approaches, in which other potential product channels (for example, CO, CO<sub>2</sub>) are monitored and other parameters (*e.g.* pressure) are varied would offer further mechanistic insights.

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