

# Measurements of OH and HO<sub>2</sub> yields from the gas phase ozonolysis of isoprene

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**Abstract.** The reactions of ozone with alkenes are an important source of hydroxyl (OH) radicals; however, quantification of their importance is hindered by uncertainties in the absolute OH yield. Hydroxyl radical yields for the gas-phase ozonolysis of isoprene are determined in this paper by four different methods: (1) The use of cyclohexane as an OH scavenger, and the production of cyclohexanone, (2) The use of 1,3,5-trimethylbenzene as an OH tracer, and the diminution in its concentration, (3) A kinetic method in which the OH yield was obtained by performing a series of pseudo-first-order experiments in the presence or absence of an OH scavenger (cyclohexane), (4) The OH and HO<sub>2</sub> yields were determined by fitting the temporal OH and HO<sub>2</sub> profiles following direct detection of absolute OH and HO<sub>2</sub> concentrations by laser induced fluorescence at low pressure (Fluorescence Assay by Gas Expansion- FAGE). The following OH yields for the ozonolysis of isoprene were obtained, relative to alkene consumed, for each method: (1) Scavenger (0.25±0.04), (2) Tracer (0.25±0.03), (3) Kinetic study (0.27±0.02), and (4) Direct observation (0.26±0.02), the error being one standard deviation. An averaged OH yield of 0.26±0.02 is recommended at room temperature and atmospheric pressure and this result is compared with recent literature determinations. The HO<sub>2</sub> yield was directly determined for the first time using FAGE to be 0.26±0.03.

nised as a major source of organic acids and organic hydroperoxides in the atmosphere (Horie et al., 1994; Becker et al., 1993, 1990; Baker et al., 2002; Gäb et al., 1995; Hewitt and Kok, 1991; Moortgat et al., 2002; Neeb et al., 1997; Sauer et al., 1999; Simonaitis et al., 1991) and the ozonolysis of biogenic alkenes, typically terpenes, has been known to form particulate products which serve as the precursors to secondary organic aerosols (Donahue et al., 2007). Finally, the reaction provides a direct means for the oxidation of unsaturated non-methane hydrocarbons (NMHC) that competes with OH radical and NO<sub>3</sub> radical initiated processes which also give rise to intermediates that are of atmospheric significance. For example, products of the ozonolysis of isoprene include methyl vinyl ketone (MVK), methacrolein and formaldehyde. Since the reactions can occur throughout the night as well as during the day, their importance is further enhanced. Intermediates arising from ozone-alkene chemistry in the gas phase are believed to include a carbonyl oxide species, the Criegee intermediate (C.I.), which can further react with tropospheric trace constituents to form aerosols (e.g., C.I. + SO<sub>2</sub>→SO<sub>3</sub>→sulfate aerosols) (Asatryan and Bozzelli, 2008; Docherty and Ziemann, 2003; Donahue et al., 2007) or phytotoxic species (e.g., C.I. + H<sub>2</sub>O→hydroxymethylhydroperoxide) (Neeb et al., 1997).

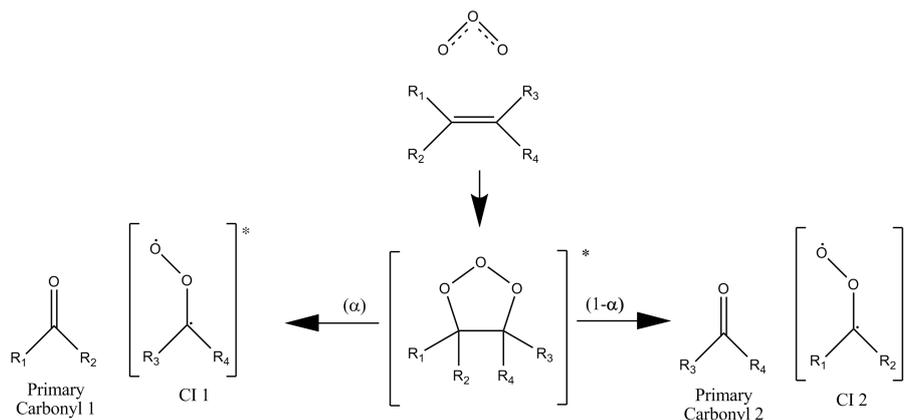
It has generally been accepted that ozone-alkene reactions in the gas phase also give rise to the production of OH radicals (Johnson and Marston, 2008). Although this proposition has been questioned (Schafer et al., 1997), laboratory based experiments (Kroll et al., 2001a, 2001b; Marston et al., 1998; McGill et al., 1999; Paulson et al., 1997) have confirmed beyond reasonable doubt that OH radicals are indeed formed in these reactions. Calculations indicate that the reactions are not only the major tropospheric source of OH at night but may even be the dominant source during the daytime where the concentration of anthropogenic alkenes is high, for example in an urban environment, and may also significantly

## 1 Introduction

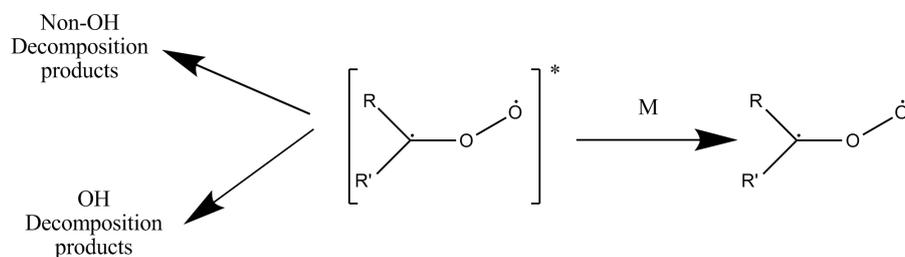
The gas-phase reactions of ozone with alkenes are important atmospheric radical sources, the main focus of this paper, but also play other important roles in the chemistry of the Earth's troposphere. The reactions have been recog-



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**Fig. 1.** Ozonolysis initiation: [3+2] cycloaddition of ozone to the alkene double bond. \* indicates the excited intermediate.



**Fig. 2.** Stabilization or decomposition of the Criegee Intermediate.

affect the atmospheric chemistry of rural air (Paulson and Orlando, 1996).

Isoprene is emitted in large quantities by biogenic sources and is sufficiently reactive to influence oxidant levels over large portions of the continental troposphere. Isoprene is emitted into the troposphere in greater quantities than any other non-methane hydrocarbon. The annual global VOC flux is estimated to be 1150 Tg C, 44% of which is isoprene (Arneth et al., 2008; Guenther et al., 1995). Isoprene emissions generally only affect lower troposphere and boundary layer chemistry. Isoprene is only emitted during the hours of daylight and has a short lifetime of approximately 1.5 h (for  $[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$ ) (Atkinson and Arey, 2003) meaning that very little, if any, isoprene escapes from the boundary layer. For example, Kesselmeier et al. (2000) measured vertical profiles of isoprene (and some monoterpenes) over pristine forest in Amazonia. The lowest mixing ratios were found at the highest altitudes (500 m), and the largest at the surface, the latter exhibiting considerable diurnal variation.

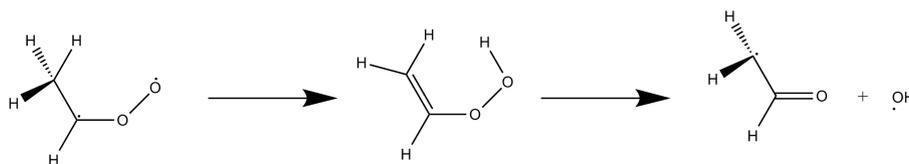
Ozonolysis is an important daytime source of OH. During the TORCH campaign in summer 2003 (25 miles NE of London), isoprene was the main biogenic NMHC constituent with an average concentration of 0.1 ppb and a maximum concentration of 1.3 ppb (Lee et al., 2006). During this campaign the rate of OH production from ozonolysis

of alkenes (between 11:00 a.m. and 03:00 p.m., GMT) was  $2.1 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$ . Even in the daytime the  $\text{O}_3$ +alkenes reactions represented an important source of OH comparable with the  $J(\text{O}^1\text{D})$  source (rate of OH production from ozone photolysis was  $3.1 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$  for a comparable period) in urban areas (Emmerson et al., 2007).

The mechanisms of gas-phase ozone-alkene reactions are complex. The basis of the current understanding was provided by Criegee and Wenner (1949) and has most recently been reviewed by Johnson and Marston (2008). The initiation involves the concerted [3+2] cycloaddition of ozone to the double bond of the alkene forming a cyclic 1,2,3-trioxolane intermediate species (also known as the primary ozonide). The primary ozonide then rapidly decomposes to give a pair of Criegee Intermediates (C.I.) and carbonyl compounds (in the case of symmetric alkenes, only one C.I. and one carbonyl compound are formed) (Fig. 1).

The C.I. may then be collisionally stabilized or decompose. It is this decomposition of the excited C.I. that can give rise to OH radicals, in addition to other products (Fig. 2).

The decomposition products of the C.I. depend on the substitution of the C.I.s. The simplest C.I. possible is  $\bullet\text{CH}_2\text{OO}\bullet$ , which is formed during the ozonolysis of ethene and terminal alkenes, or the C.I. may be either monosubstituted ( $\text{R}\bullet\text{CHOO}\bullet$ ) or disubstituted ( $\text{RR}'\bullet\text{COO}\bullet$ ). It was



**Fig. 3.** Martinez and Herron (1988), hypothesis of OH radical production from a 1,4-sigmatropic shift within the CI, followed by bond fission.

**Table 1.** Previous measurements of the OH yield for the ozonolysis of isoprene.

Reference	OH yield	Technique
Aschmann et al. (1996)	0.27	Cyclohexane scavenger
Donahue et al. (1998)	0.50	LIF of OH at 5 Torr
Gutbrod et al. (1997)	0.19	CO scavenger
International Union of Pure and Applied Chemistry (2005)	0.25	Recommendation (evaluated)
Lewin et al. (2001)	0.59 0.45 0.55	2-Butanol scavenger, Trimethyl benzene (TMB) tracer <i>m</i> -xylene tracer
Master Chemical Mechanism (MCM), Version 3.1	0.27	Value used by models
Neeb and Moortgat (1999)	0.26	Cyclohexane scavenger
Paulson et al. (1992)	0.68	Methylcyclohexane scavenger
Paulson et al. (1998)	0.26	Tracer pair
Rickard et al. (1999)	0.44	TMB tracer
Zhang et al. (2002)	0.25	Statistical-dynamical master equation

hypothesised by Martinez and Herron (1988) that OH radical production can result from a 1,4-sigmatropic shift within the C.I. followed by bond fission (Fig. 3). This isomerisation requires that the alkyl-substituent group is on the same side of the C.I. as the terminal O atom (syn conformation).

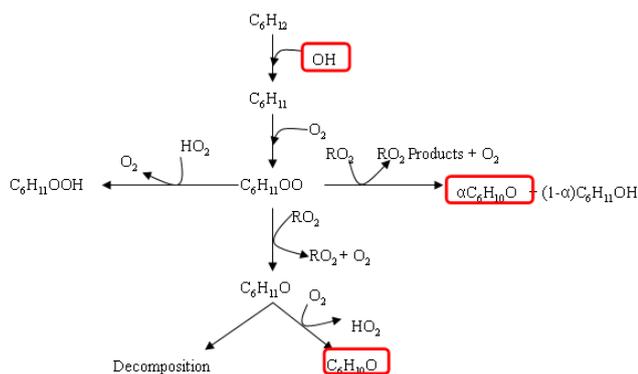
Due to the abundance of isoprene, the ozonolysis of isoprene represents an important source of tropospheric hydroxyl radicals, although significant controversy remains over the relative role of OH production from the nascent (excited) versus stabilized C.I., and also over the absolute yields (Kroll et al., 2001a, 2001b). Several studies of stable products from the ozonolysis of isoprene have been reported (e.g. Kamens et al., 1982; Hasson et al., 2001). Table 1 summarizes the studies which have reported OH yields, from which it can be seen that the measured yields of hydroxyl radicals are extremely varied. Uncertainty in the absolute yields hinders mechanistic analysis.

In this paper we report a determination of OH yields using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) (Glowacki et al., 2007a). One of the major advantages of HIRAC is the ability to directly measure absolute OH and HO<sub>2</sub> radical concentrations using the FAGE (Fluorescence Assay by Gaseous Expansion) technique (Heard, 2006). A variety of indirect techniques, as well as direct observation of OH, has been used to provide a consistent

measurement of the OH yield from the reaction of ozone with isoprene. The indirect methods used were analysis of the amount of product (cyclohexanone) produced in the presence of an OH scavenger (cyclohexane) (Aschmann et al., 1996), studies on the consumption of a tracer species, trimethyl benzene (TMB) (Rickard et al., 1999) and observing the variation in the kinetics of isoprene removal in the presence/absence of an OH scavenger (Neeb and Moortgat, 1999). In subsequent experiments temporal profiles of OH and HO<sub>2</sub> were measured using the FAGE technique with OH and HO<sub>2</sub> yields determined from numerical simulations of the radical profiles based on the Master Chemical Mechanism (MCM) (Jenkin et al., 2003).

## 2 Experimental

**HIRAC** – All the studies were performed in HIRAC, a cylindrical reaction chamber with internal dimensions 2000 mm (length) and 1200 mm (diameter) and a volume of  $\sim 2.250 \text{ m}^3$ , and a surface to volume ratio of  $\sim 5.8 \text{ m}^{-1}$ . The chamber was constructed from grade 304 stainless steel to enable pressure and temperature variation and to allow mounting/access holes and instrumentation ports to be easily cut into the skin during manufacture. The HIRAC skin features a set of entry points or flanges. These flanges include



**Fig. 4.** Production of cyclohexanone from OH + cyclohexane.

various holes for placing windows for coupling to the FTIR beam, introducing gas chromatograph (GC) and trace-gas analyser box sampling lines, four 500 mm access ports, two in one side to set up the FAGE calibration or clean the chamber and one on either end, and six smaller access flanges for coupling HIRAC to the FAGE system or other instrumentation. HIRAC contains mounting points for four rotary feed-through fans.

Pressures were measured using two types of pressure gauges: Leybold Ceravac CTR90 (0–1000 Torr) and Leybold Thermovac TTR91 (Pirani type gauge). HIRAC was evacuated between experiments and the chamber could be pumped from ambient pressure to  $\sim 2.5 \times 10^{-3}$  mbar within  $\sim 70$  min using a combination of a rotary pump (Leybold Trivac D40B) backed roots blower (Leybold Ruvac WAU251) with a charcoal filled catchpot (BOC Edwards, ITC300) trap to avoid oil backflush into the evacuated chamber (Glowacki et al., 2007a).

**Reagent Preparation** – A mixture of isoprene and the relevant hydroxyl radical scavenger/tracer was prepared in a 1 L stainless steel mixing vessel and flushed into the HIRAC chamber with a stream of nitrogen. Typical initial concentrations in HIRAC were between 1–10 ppmv (volume fraction in ppm) of isoprene, 60–300 ppmv of cyclohexane and from 1–10 ppmv of TMB. Typical initial ozone mixing ratios ranged from ca. 0.5–8 ppmv. Ozone was generated within the HIRAC chamber by a suspended mercury pen-ray lamp (Oriol Spectra-Physics, 6035) prior to the introduction of the alkene. All reagents employed were of analytical grade and underwent freeze-pump-thaw cycles before being used. Synthetic air (BOC, BTCA 178) was used as the bath gas in these experiments. During experiments gas from HIRAC was sampled by various instruments; a known flow of synthetic air was introduced to maintain the pressure at  $\sim 1$  atm. Throughout the experiments, all four of HIRAC's fans were run at 50% of their maximum speed (1500 rpm, maximum speed is 3000 rpm) giving an approximate mixing time of 70 s.

**Experimental procedure** – Experiments were carried out generating a known concentration of ozone within the

HIRAC chamber, and adding a sample of the hydrocarbon mixture such that a total chamber pressure of  $\sim 1$  atm ( $1000 \pm 10$  mbar) was achieved. The mixing of reactants was sufficiently ( $< 70$  s) fast on the time scale of the reactions studied. The rate of O<sub>3</sub> decay in the dark chamber in the absence isoprene was measured before and after several experimental runs, and was found to be proportional to [O<sub>3</sub>], with a unimolecular loss rate determined to be  $\sim 3.2 \times 10^{-5}$  s<sup>-1</sup>. Experiments were carried out at  $296 \pm 3$  K.

Ozone concentrations were determined by a conventional UV photometric O<sub>3</sub> analyzer (Thermo Electron Environmental instruments, Model 49C), which had a detection limit of 1.0 ppb, a standard sample flow rate of 2 L/min, a response time of 20 s with a 10 s averaging time. The O<sub>3</sub> analyser had been calibrated using a commercial ozone primary standard (Thermo Electron Corporation 49i-PS) and an intercomparison with the FTIR was linear (Glowacki et al., 2007a, 2007b).

The hydrocarbons were detected by GC-FID (Flame Ionisation Detection, Agilent Technologies 6890N) employing a 30 m, 0.32 mm i.d. column coated with 5% phenyl methyl siloxane (J&W, HP-5) and held isothermally at 160 °C.

In some experiments, the decay of isoprene was also monitored by FTIR between 1500–1700 cm<sup>-1</sup> and 800–950 cm<sup>-1</sup>. HIRAC contains a long path IR absorption facility. IR radiation from a Bruker IFS 66 spectrometer was coupled into HIRAC using a set of transfer optics housed in a nitrogen purged Perspex box. The windows for IR ingress and exit were wedged CaF<sub>2</sub>. Inside HIRAC a multipass modified Chernin cell has been constructed which was optimised for 72 internal reflections giving an approximate path length of 144 m (Glowacki et al., 2007b). On exiting the chamber the IR radiation was focused into an externally mounted MCT detector connected to the spectrometer, also mounted in the purged box.

**Detection of OH and HO<sub>2</sub> using the FAGE technique** – A continuous sample of chamber air ( $\sim 2$  L min<sup>-1</sup>) was drawn through a 0.8 mm diameter pinhole at the apex of a conical inlet, positioned close to the centre of the HIRAC chamber. Following a free-jet supersonic expansion, the flow becomes subsonic and travels down a black anodized aluminium flowtube (internal diameter 50 mm) into a fluorescence cell, located outside of the HIRAC chamber, and maintained at  $1.2 \pm 0.1$  Torr by a rotary pump backed roots blower combination (Leybold Trivac D40B and Ruvac WAU251). OH radicals were excited by a pulsed laser at approximately 308 nm ( $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_i(v''=0)$  Q<sub>1</sub> transition,  $307.995 \pm 0.001$  nm), with detection of resonant fluorescence perpendicular to both the probe laser and gas flows (Glowacki et al., 2007a). The 308 nm radiation was generated by a Nd:YAG laser (JDSU Q201-HD) pumped dye laser (Sirah Cobra stretch) operating at 5 kHz pulse repetition frequency, with a pulse length of  $< 40$  ns, pulse energy of  $> 12$  μJ and a spectral bandwidth of  $0.097 \pm 0.010$  cm<sup>-1</sup> at 308 nm. The laser radiation was transferred to the

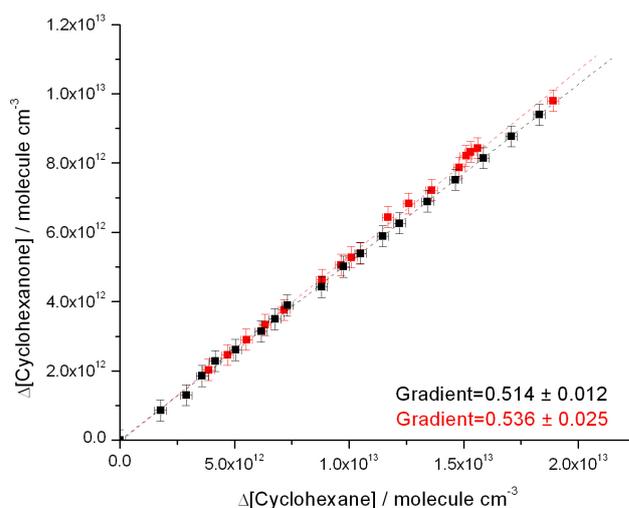
fluorescence cell by an optical fibre (length 10 m, core diameter 200  $\mu\text{m} \pm 4 \mu\text{m}$ ), and after collimation, the laser beam (10 mm diameter) crosses the gas flow 380 mm from the sampling pinhole. In the FAGE technique a low pressure is used to extend the lifetime of the OH fluorescence, allowing the fluorescence to be recorded using gated photon counting whilst discriminating against laser scattered light. The laser scattered light was minimised by using a fluorescence cell with baffled side-arms, consisting of a series of matt black plastic rings separated along the arm by spacers, and by careful imaging of only a small excitation volume at the centre of the cell onto the detector. A second, identical fluorescence cell was located 380 mm further downstream, in which HO<sub>2</sub> was detected following its conversion into OH by reaction with added NO (with a flow rate of 5 sccm).

The laser power entering each fluorescence cell was typically 5–10 mW. The fluorescence signal passed through a 1/8" thickness UV grade fused silica window (providing the pressure seal), was collimated by two plano-convex 50 mm diameter, 100 mm focal length (at 633 nm) lenses, positioned outside the cell, and then passed through a 308 nm interference filter (Barr Associates, 308.75 nm central wavelength, 5.0 nm bandwidth, 50% transmission). The fluorescence was focussed onto the photocathode of a channel photomultiplier (CPM, Perkin-Elmer C943P ca.  $5 \times 10^8$  gain) using optics identical to those used for collimation. All the optics were coated with a 308 nm anti-reflective coating, the solid-angle over which the OH fluorescence was collected was approximately doubled by using a back reflector, whose focal length was matched to that of the combination of the two plano-convex lenses. Individual photons detected by the CPM were processed by a gated photon counting (Becker and Hickl, PMS MSA 400A), and counted over an integration period of 252 ns, delayed by 450 ns from the laser pulse. The gain of the CPM was switched to zero during the laser pulse using a home-built gating system in order to further reduce the background signal due to laser-scattered light (Creasey et al., 1998). The signal was subsequently normalised for laser power, as measured by a photodiode (New Focus-2032) mounted at the exit of the fluorescence cell.

### 3 Results and discussion

#### 3.1 Cyclohexane as an OH scavenger

This method was first described by Atkinson et al. (1996, 1989). The reaction of isoprene with ozone was performed in the presence of excess cyclohexane in synthetic air. The concentration of cyclohexane (60–150 ppm) was sufficient to scavenge >95% of the OH produced. The products of the OH radical reaction with cyclohexane (cyclohexanol and cyclohexanone) were monitored as a function of time by a GC-FID which had previously been calibrated with known standards. The decay of isoprene relative to the production



**Fig. 5.** Yield of cyclohexanone from OH + cyclohexane. Errors in the gradient are standard errors ( $1\sigma$ ) obtained in the regression analysis. Error bars are the associated errors from the GC calibration of cyclohexane and cyclohexanone.

of cyclohexanone was used to determine the OH yield ( $Y_{\text{OH}}$ ) of the ozone reaction with isoprene; however it was first required to verify the yield of cyclohexanone from OH initiated oxidation of cyclohexane.

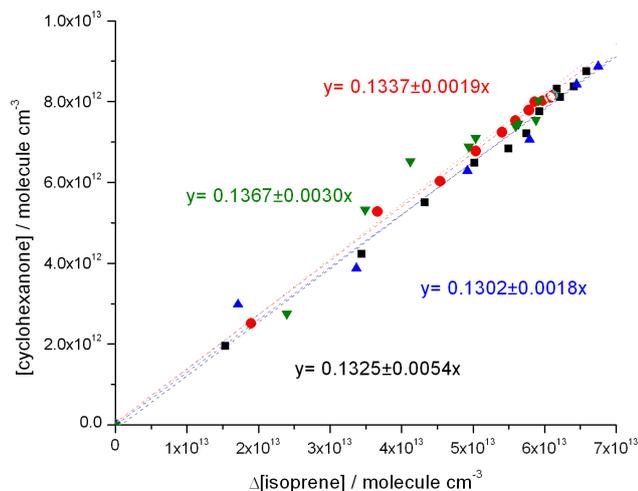
The reaction of OH with cyclohexane produces cyclohexanone in (50 $\pm$ 5) % yield (Atkinson and Aschmann, 1993; Shu and Atkinson, 1994). This reaction has been used by Atkinson and Aschmann to determine OH yields for a number of ozonolysis reactions. In order to determine the OH yield, the yield of cyclohexanone produced from the reaction of OH with cyclohexane is required. The literature yield was verified in two ways using two different OH sources:

1. The production of OH by isoprene ozonolysis. Low concentrations of cyclohexane were used so the loss of cyclohexane was comparable to the production of cyclohexanone, as shown in Fig. 5 (red points), and allowing the yield to be determined.
2. The production of OH from methyl nitrite. The loss of cyclohexane compared to the production of cyclohexanone was again determined, as shown by the black points in Fig. 5.

The average cyclohexanone yield from cyclohexane oxidation using the two sources of OH was found to be  $0.525 \pm 0.020$ , and is in good agreement with previous values of 0.5 (Atkinson et al., 1996). The reaction of isoprene with ozone was performed in the presence of excess cyclohexane

**Table 2.** OH yields for ozonolysis of isoprene using cyclohexane scavenger, errors quoted are standard errors obtained in the regression analysis. Errors are determined from a propagation of errors from the cyclohexanone yield and the gradients in Fig. 6 ( $1\sigma$ ).

Expt. No.	Cyclohexane: Isoprene	Conditions	[cyclohexanone] / $\Delta$ [isoprene]	OH Yield
1 (blue)	500:1	Isoprene 3 ppm Ozone 3 ppm Cyclohexane 1500 ppm	0.1302±0.018	0.248±0.035
2 (black)	500:1	Isoprene 3 ppm Ozone 3 ppm Cyclohexane 1500 ppm	0.1325±0.025	0.252±0.041
3 (green)	Isoprene 3 ppm 500:1	Ozone 3 ppm Cyclohexane 1500 ppm	0.1367±0.030	0.260±0.057
4 (red)	250:1	Isoprene 3 ppm Ozone 3 ppm Cyclohexane 750 ppm	0.1337±0.019	0.255±0.036
			Average	0.253±0.042



**Fig. 6.** Plot of cyclohexanone concentration with respect to that of change of isoprene to identify the OH yield, obtained under different experimental conditions.

(250–500 fold excess) in synthetic air. The yield of OH from O<sub>3</sub> plus isoprene,  $Y_{OH}$ , was then determined from:

$$Y_{OH} = \frac{[\text{cyclohexanone}]/\Delta[\text{isoprene}]}{[\text{cyclohexanone}]/\Delta[\text{cyclohexane}]} \quad (1)$$

$$= \frac{[\text{cyclohexanone}]/\Delta[\text{isoprene}]}{0.525}$$

The ratio of cyclohexane to isoprene was varied with no discernable influence on the OH yield. A typical plot of [cyclohexanone] vs.  $\Delta$ [isoprene], is shown in Fig. 6. The OH

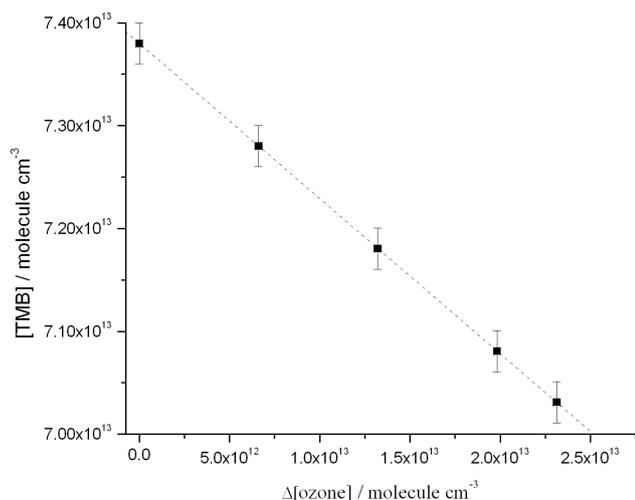
**Table 3.** Experimental conditions for 1,3,5 TMB scavenger study.

Expt. No.	[O <sub>3</sub> ] / ppm	[1,3,5 TMB] / ppm	[Isoprene] / ppm
1	1.02	3.21	9.10
2	2.10	3.12	3.00
3	2.23	6.04	3.51
4	1.03	3.31	3.12
5	3.01	3.12	12.03
6	3.10	2.97	6.12
7	1.99	2.89	6.01
8	1.98	3.20	5.98
9	2.12	3.02	6.14

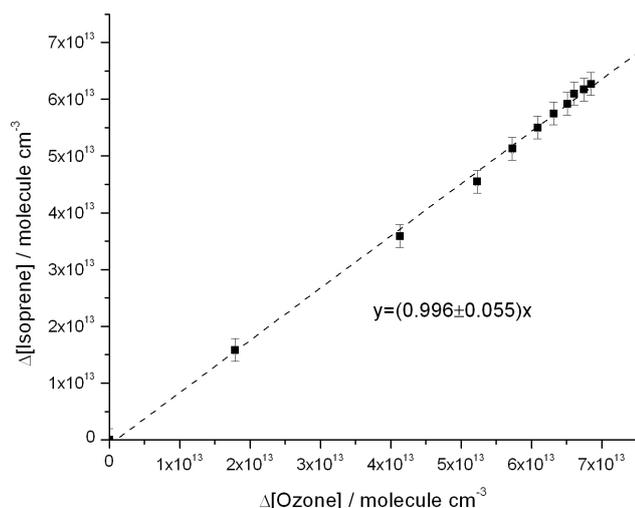
formation yields from ozone plus isoprene was then obtained from Eq. (1), and the results are summarized in Table 2.

### 3.2 1,3,5-trimethylbenzene as an OH tracer

The principle of this method has been described by Lewin et al. (2001); Rickard et al. (1999); these experiments involve the ozonolysis of isoprene in the presence of a hydroxyl radical tracer, 1,3,5-trimethylbenzene (TMB), which reacts relatively quickly with OH ( $k=(5.75\pm 0.91)\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson and Aschmann, 1989) but does not react with ozone under the conditions of the experiments ( $k=(3\pm 2)\times 10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) (Kramp and Paulson, 1998) where the concentration of isoprene is always in excess of ozone. Hence the product of  $k_{O_3+TMB}[O_3]=2.2\times 10^{-7}$  s<sup>-1</sup>



**Fig. 7.** Plot of concentration of TMB with respect to the change of ozone concentration, the gradient is equal to  $\frac{-k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0 + k_{\text{loss}}}\beta$ . The error in each point and the gradient represents  $1\sigma$ .



**Fig. 8.** Change of ozone concentration relative to that of isoprene to identify the reaction stoichiometry, [cyclohexane]=1500 ppm. The error in each point and the gradient represents  $1\sigma$ . The error in the ordinate axis is small compared to the symbol size.

compared to  $k_{\text{OH}+\text{TMB}}[\text{OH}] = 1060.9 \text{ s}^{-1}$ , when assuming that all the ozone (in this example 3 ppm) reacts with the excess isoprene and has an OH yield of  $\sim 0.25$ .

OH yields were determined by monitoring [TMB], using GC-FID, as a function of the change in ozone concentration,  $\Delta[\text{O}_3]$ . Isoprene was in excess over ozone, and the reactants were left long enough that the initial concentration of ozone was equal to  $\Delta[\text{O}_3]$ . If the OH yield (relative to ozone consumption) for a given ozonolysis reaction is  $\beta$ , the total concentration of OH formed in an experiment is given by

**Table 4.** An example of the reproducibility of 1,3,5 TMB (3 ppm) and Isoprene (6 ppm) GC injections.

Injection No.	[1,3,5 TMB] / $\times 10^{13}$ molecule $\text{cm}^{-3}$	[Isoprene] / $\times 10^{13}$ molecule $\text{cm}^{-3}$
1	7.38	14.76
2	7.36	14.76
3	7.37	14.75
4	7.38	14.74
5	7.38	14.78
6	7.40	14.78
7	7.39	14.76
8	7.38	14.74
9	7.38	14.76
10	7.37	14.77

$\beta \Delta[\text{O}_3]$ . The magnitude of the change in [TMB] is given by  $f \beta \Delta[\text{O}_3]$ , where  $f$  is the fraction of the OH formed that reacts with TMB:

$$f = \frac{\text{rate of reaction OH}+\text{TMB}}{\text{total rate of OH removal}} \quad (2)$$

$$= \frac{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0 + k_{\text{loss}}}$$

Here we are assuming the concentration of the excess isoprene does not change.

$$[\text{TMB}]_0 = [\text{TMB}] + \frac{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0 + k_{\text{loss}}}\beta \Delta[\text{O}_3] \quad (3)$$

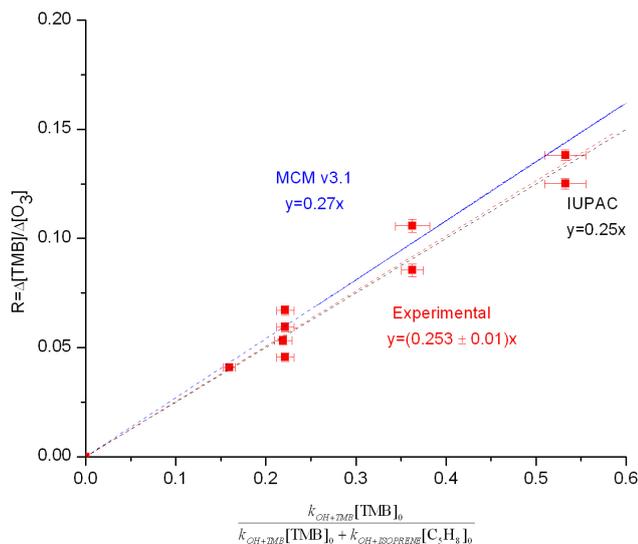
where  $[\text{TMB}]_0$  is the initial concentration of TMB and  $k_{\text{loss}}$  is a first-order rate constant representing other loss processes for OH, such as reaction with products. A plot of [TMB] vs.  $\Delta[\text{O}_3]$  will give a straight line with a slope of:

$$\frac{-k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0 + k_{\text{loss}}}\beta$$

as shown in Fig. 7. Figure 7 shows that the precise measurements of the hydrocarbon are required in order to extract the yield; the requisite reproducibility of the GC analysis is demonstrated in Table 4.

The parameter  $\beta$  is the OH yield relative to ozone consumption, whereas most previous reports quote the yield relative to isoprene consumption,  $\alpha \equiv Y_{\text{OH}}$ , the desired quantity here. To convert  $\beta$  to  $\alpha$ , it is necessary to simply divide by the reaction stoichiometry,  $\Delta[\text{isoprene}]/\Delta[\text{ozone}]$ . The stoichiometries were measured in separate experiments under ‘‘OH-free’’ conditions (in excess cyclohexane), and were determined as the gradient of  $\Delta(\text{O}_3)$  plotted against  $\Delta[\text{C}_5\text{H}_8]$ , as shown in Fig. 8. For this study the stoichiometry was found to be  $1.00 \pm 0.05$ .

For very small values of  $\Delta[\text{O}_3]$ ,  $k_{\text{loss}} \approx 0$  because product concentrations are very small and wall losses for OH are expected to be small compared to reaction with the alkene and



**Fig. 9.** Analytical treatment of experimental results using 1,3,5 TMB as an OH tracer. The gradient determines the OH yield as discussed in the text. Errors in the abscissa and ordinate axis are calculated from propagation of errors and are quoted as  $1\sigma$ . The gradient error is the standard error obtained in the weighted regression analysis. The red plot is the experimentally determined value of  $\beta$  ( $\beta$ =OH yield with respect to ozone consumption).  $\alpha$ =OH yield with respect to Isoprene consumption).  $\beta$ /reaction stoichiometry= $\alpha$ . In this case the reaction stoichiometry equals 1 hence  $\beta=\alpha$ . The blue plot is generated using the recommended MCM v.3.1 OH yield and the black plot is generated using the IUPAC recommended OH yield.

TMB. For larger values of  $\Delta[\text{O}_3]$ , the TMB and alkene terms in the denominator of Eq. (2) decrease but are at least partially compensated for by increases in  $k_{\text{loss}}$  due to the reaction of OH with products. The fact that no curvature is observed in plots of  $[\text{TMB}]$  vs.  $\Delta[\text{O}_3]$  (Fig. 7) indicates that the slope of such plots is given by:

$$\frac{-k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0} \beta$$

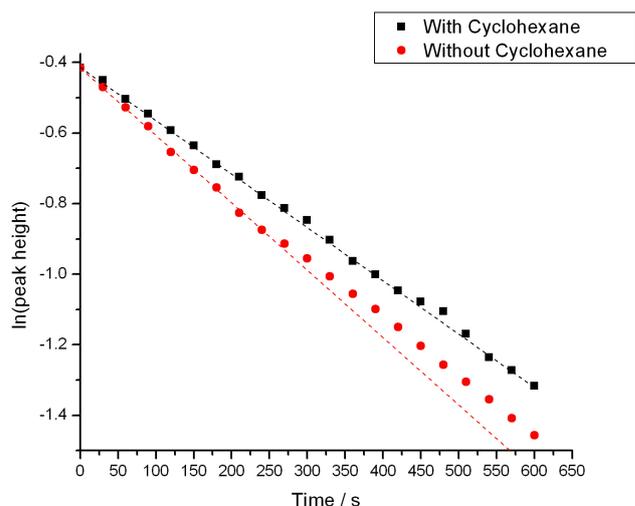
and hence OH yields relative to ozone consumed are readily obtained. Plots of  $\Delta[\text{TMB}]/\Delta[\text{O}_3]$  vs.

$$\frac{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0}{k_{\text{OH}+\text{TMB}}[\text{TMB}]_0 + k_{\text{OH}+\text{ISOPRENE}}[\text{C}_5\text{H}_8]_0}$$

are linear, and reproducible, as shown in Fig. 9. The amount of TMB and isoprene reacted were measured using GC-FID with absolute concentrations determined using a multipoint calibration. The concentration of the ozone reacted was monitored using a commercial ozone analyser, which had recently been calibrated. From Figure 9, the gradient gave the OH yield,  $Y_{\text{OH}}=0.25\pm 0.01$ .

### 3.3 Cyclohexane kinetic study

This method was first described by Neeb and Moortgat (1999). Experimental conditions ensure the decay of iso-

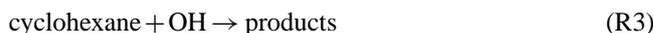


**Fig. 10.** Profile of  $\ln(\text{isoprene peak height})$  vs time using FTIR.

prene follows pseudo first order kinetics using a 10 fold excess of ozone over isoprene. The consumption of isoprene was monitored using both FTIR and GC-FID methods, with the decrease in the isoprene signals described in all cases by an exponential decay:

$$[\text{isoprene}]_t = [\text{isoprene}]_0 \exp(-k'_{\text{obs}}t)$$

The analysis is based on the following reactions:



Products formed in these reactions also react with OH radicals, thus diminishing the consumption of the isoprene by reaction 2 at later stages of the reaction, hence only the first 5 points of the isoprene decay (as shown in Figure 10) were used to determine the pseudo first order rate constant,  $k'_{\text{obs}}$ , which is related to the bimolecular rate constant,  $k_{\text{eff}}$  by:

$$k'_{\text{obs}} = k_{\text{eff}}[\text{O}_3] \quad (4)$$

In the presence of sufficient concentrations of cyclohexane to scavenge virtually all the OH, the isoprene is removed solely by reaction with ozone, and the experimentally determined effective rate constant,  $k'_{\text{obs}}$  from the pseudo first order decay (Fig. 10) is equal to  $k_{\text{O}_3+\text{ISOPRENE}}[\text{O}_3]$ . When there is no cyclohexane present, isoprene decays more quickly due to reaction (R2) (Fig. 10), and  $k_{\text{eff}}$  increases. From  $k_{\text{eff}}$  measured under these conditions the yield of OH radicals is directly related to  $k_{\text{eff}}$  by:

$$Y_{\text{OH}} = (k_{\text{eff}} - k_{\text{O}_3+\text{ISOPRENE}})/k_{\text{O}_3+\text{ISOPRENE}} \quad (5)$$

**Table 5.** Experimental conditions for cyclohexane kinetic study.

Cyclohexane free Conditions	Cyclohexane added conditions	OH yield	
		FTIR	GC
[O <sub>3</sub> ]=10 ppm [Isoprene]=1 ppm	[O <sub>3</sub> ]=10 ppm [Isoprene]=1 ppm [Cyclohexane]=100 ppm	0.260±0.015	0.265±0.020
[O <sub>3</sub> ]=10 ppm [Isoprene]=1 ppm	[O <sub>3</sub> ]=10 ppm [Isoprene]=1 ppm [Cyclohexane]=100 ppm	0.270±0.020	0.275±0.020
[O <sub>3</sub> ]=5 ppm [Isoprene]=0.5 ppm	[O <sub>3</sub> ]=5 ppm [Isoprene]=0.5 ppm [Cyclohexane]=100 ppm	0.255±0.015	0.255±0.020
[O <sub>3</sub> ]=5 ppm [Isoprene]=0.5 ppm	[O <sub>3</sub> ]=5 ppm [Isoprene]=0.5 ppm [Cyclohexane]=100 ppm	0.265±0.015	0.275±0.020
[O <sub>3</sub> ]=7.5 ppm [Isoprene]=0.75 ppm	[O <sub>3</sub> ]=7.5 ppm [Isoprene]=0.75 ppm [Cyclohexane]=100 ppm	0.265±0.015	0.265±0.020
Average Yield		0.263±0.015	0.267±0.020
		0.27±0.02	

where  $Y_{\text{OH}}$  corresponds to the yield of the OH radical formed in the isoprene ozonolysis reaction. During the early stages of the reaction, OH radicals will almost exclusively react with isoprene or cyclohexane, if present. It should be also pointed out that the OH radical yield ( $Y_{\text{OH}}$ ) represents an overall yield that also includes a possible contribution from the reaction of the HO<sub>2</sub> radical with O<sub>3</sub>.



with HO<sub>2</sub> radicals formed from the decomposition channels of the excited Criegee intermediate CH<sub>2</sub>OO\* in the presence of O<sub>2</sub>. Another source of HO<sub>2</sub> radicals are reactions of O<sub>2</sub> with alkoxy radicals, which are formed in peroxy radical reactions of the products formed in reactions 1-3. The occurrence of reaction (R4) is a potential complication to the determination of the OH radical yield obtained in this study. However, as shown in modelling section below, in which the rate of production of OH from various sources is compared (for example the ozonolysis of isoprene and reaction (R4)), reaction (R4) is of minor importance.

Our determination of  $k_{\text{O}_3+\text{ISOPRENE}}$  made in the presence of excess cyclohexane is in good agreement with recent previous studies (Table 6). The OH yields determined by this technique are  $Y_{\text{OH}}=0.265\pm0.020$  using GC-FID to monitor the decay of isoprene, and  $Y_{\text{OH}}=0.260\pm0.015$  using FTIR, and are in good agreement with the value of 0.26 obtained by Neeb and Moortgat using this method (Neeb and Moortgat, 1999). This technique has been used by Neeb and Moortgat to determined yields for propene, isoprene and isobutene that compared well with yields measured by Atkinson and Paulson.

**Table 6.** Rate Constants for the Reaction of ozone with isoprene.

$k_{\text{O}_3}$ [cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ]	
$(1.23\pm0.02)\times10^{-17}$	this work
$(1.19\pm0.09)\times10^{-17}$	Klawatsch-Carrasco et al. (2004)
$1.33\times10^{-17}$	Khamaganov and Hites (2001)
$1.30\times10^{-17}$	Neeb and Moortgat (1999)
$1.27\times10^{-17}$	Treacy et al. (1992)
$1.22\times10^{-17}$	Greene and Atkinson (1992)
$9.6\times10^{-18}$	Karl et al. (2004)

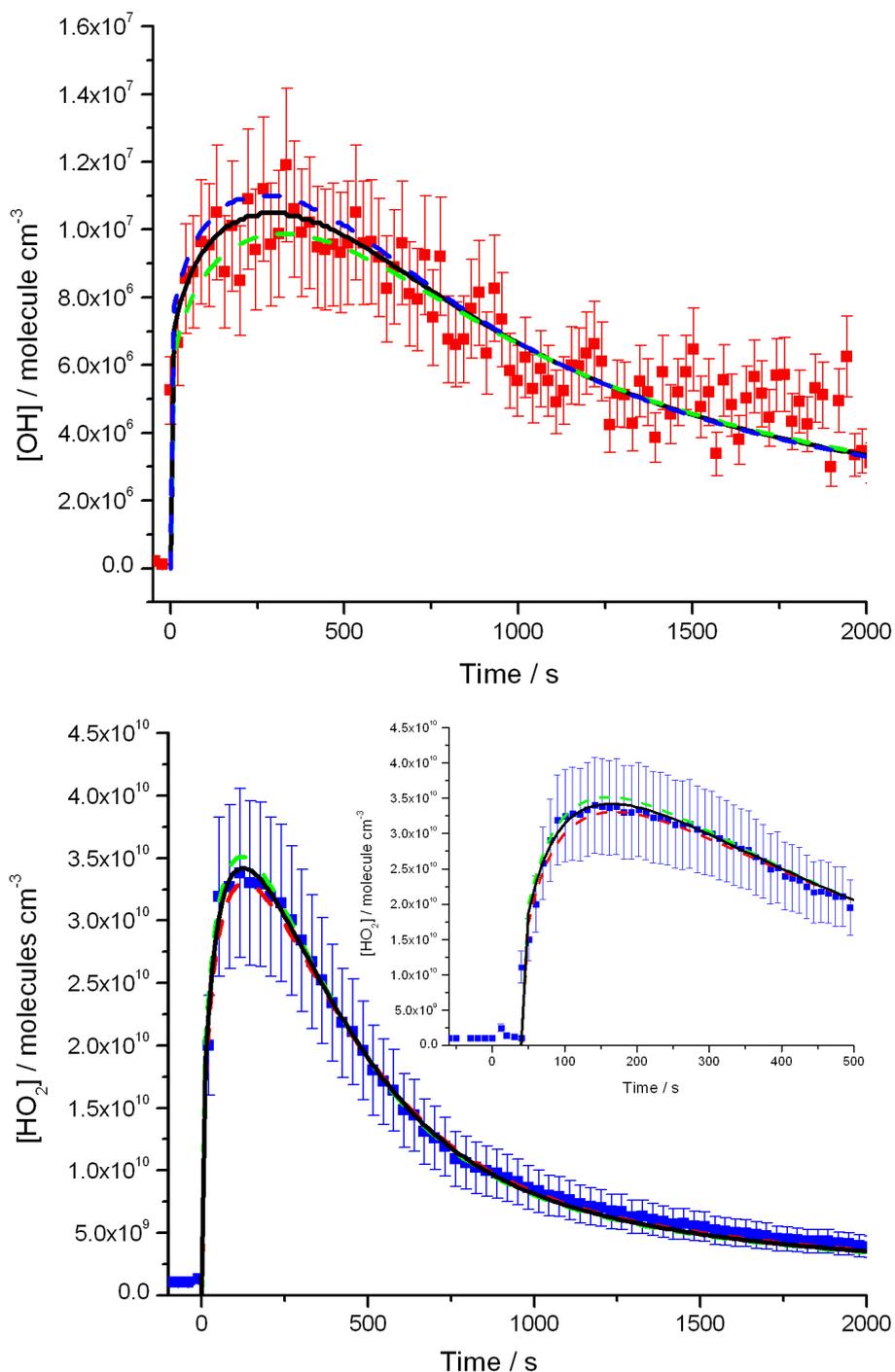
**Table 7.** Experimental conditions for direct OH and HO<sub>2</sub> detection.

[O <sub>3</sub> ] / ppm	[Isoprene] / ppm	OH Yield	HO <sub>2</sub> Yield
8.2	1.05	0.250±0.020	0.257±0.025
8.1	1	0.235±0.020	0.249±0.025
7.9	1	0.257±0.027	0.251±0.025
7.5	1	0.240±0.025	0.256±0.025
7.1	1	0.274±0.032	0.261±0.020
6.2	1	0.267±0.040	0.255±0.040
5.1	1	0.265±0.056	0.263±0.025
2.0	1	–	0.266±0.055
2.1	1	–	0.268±0.025
Average Yield		0.255±0.022	0.258±0.025

### 3.4 Direct measurement of absolute OH and HO<sub>2</sub> concentrations in HIRAC using FAGE

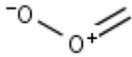
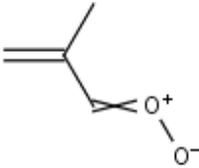
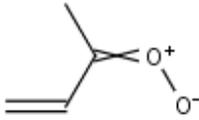
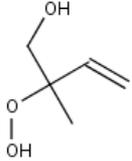
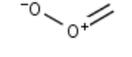
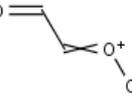
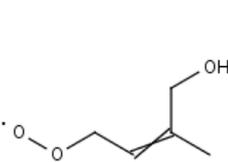
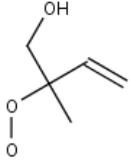
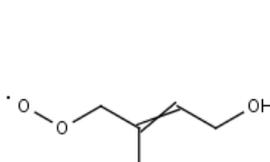
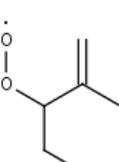
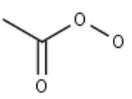
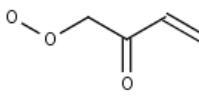
The capability of HIRAC to quantitatively measure OH radical concentrations and hence determine absolute OH yields was previously demonstrated for the reaction of O<sub>3</sub>+*t*-2-butene (Glowacki et al., 2007a), which is known to produce OH and acetaldehyde (Calvert et al., 2000; Rickard et al., 1999). A numerical model using the Master Chemical Mechanism (MCM) and constrained using other measured parameters ([*t*-2-butene], [O<sub>3</sub>]) as well as previously published OH yields from this reaction was able to reproduce the temporal profile of measured [OH], O<sub>3</sub> and acetaldehyde to within ±10% (Glowacki et al., 2007a).

An example of a time dependent OH concentration profile following initiation of the O<sub>3</sub> and isoprene reaction in synthetic air bath gas is shown in Fig. 11a. The FAGE technique was also used to make HO<sub>2</sub> measurements by means of chemical conversion to OH with NO, followed by LIF detection, and the corresponding HO<sub>2</sub> profile is shown in Fig. 11b. The HO<sub>2</sub> concentrations are much higher than OH (factor of 3000 at the peak); this is an effect of their lifetimes, the model predicts a lifetime of  $4.06\times10^{-4}$  s and 1.27 s for OH and HO<sub>2</sub> respectively (a difference of a factor of 3000). Also shown in these figures are model calculations for OH

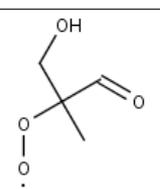
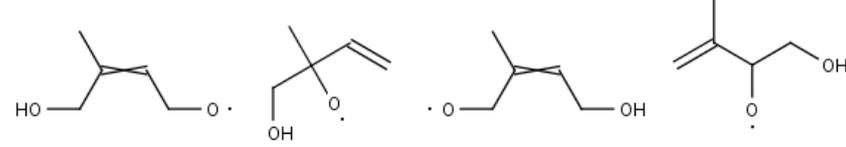
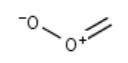
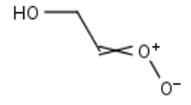
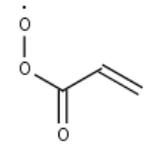


**Fig. 11.** (a) Time dependent [OH] in HIRAC generated following the reaction of O<sub>3</sub>+ isoprene, measured with the FAGE LIF instrument (20 s signal averaging, red points). The error bars are propagation of errors from the signal calibration cited as 1 $\sigma$ . The conditions of this experiment were: [O<sub>3</sub>]=8 ppm and [isoprene]=1 ppm. The solid black line is a model calculation using the MCM and a yield of OH of  $Y_{\text{OH}}=0.255$ . The blue dashed line is MCM model with OH yield of 0.324, the green dashed line is the MCM model with an OH yield of 0.216. (b) Time dependent [HO<sub>2</sub>] in HIRAC generated following the reaction of O<sub>3</sub>+ isoprene, measured with the FAGE LIF instrument (10 s signal averaging, only every third point is shown for clarity, blue points). The conditions of this experiment were: [O<sub>3</sub>]=8 ppm and [isoprene]=1 ppm. The solid black line is a model calculation using the MCM v3.1 and a yield of HO<sub>2</sub> of  $0.263\pm 0.025$ . The error bars are propagation of errors from the signal calibration cited as 1 $\sigma$ . The green dashed line is the HO<sub>2</sub> yield of 0.316 and the red dashed line is the HO<sub>2</sub> yield of 0.210. Inset shows the first 500 s of the HO<sub>2</sub> trace; this is where the greatest affect on varying the HO<sub>2</sub> yield occurs.

**Table 8.** ROPA/RODA modelling abbreviation for compounds and radicals.

Compound/Radical	ROPA Prefix
Isoprene	C5H8
Methyl Vinyl Ketone	MVK
Methacrolein	MACR
Criegee Intermediate	C.I.
Formaldehyde	HCHO
	CH2OOE
	MACROOA
	MVKOOA
	ISOPBOOH
	CH2OOB
	GLYOOE
	(ISOPO)O
	
	
	
	CH3CO3
	MVKO2

**Table 8.** ROPA/RODA modelling abbreviation for compounds and radicals.

Compound/Radical	ROPA Prefix
	MACRO2
	(ISOP)O
	CH2OOB
	GAOOB
	CH3O
	ACO3

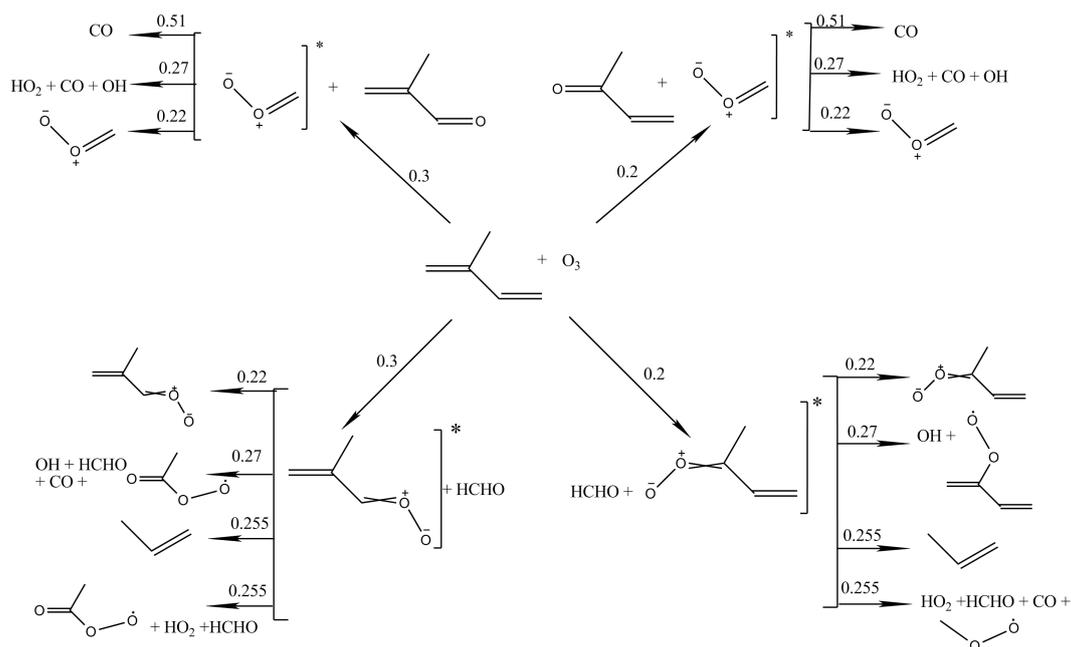
and HO<sub>2</sub> using a box-model based on the MCM (Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003) and integrated using FACSIMILE (MCPA software, Oxon, UK). The subset of the MCM extracted for these simulations included 201 species and 655 reactions. The mechanism is fully explicit for the isoprene chemistry and subsequent products. MCM v3.1 specifies that 27% of the Criegee intermediates formed from the O<sub>3</sub>+isoprene reaction yields OH, i.e. Y<sub>OH</sub>=0.27. From Fig. 11a, it can be seen that the MCM derived model using this yield fits the experimental profiles of OH and HO<sub>2</sub> very well. Treating the OH yield as a variable fitting parameter, the model was run repeatedly and an iterative least squares procedure was used to optimise the OH yield through comparison with the OH FAGE data, from which a best-fit yield of Y<sub>OH</sub>=0.255±0.022 was determined.

HO<sub>2</sub> is a product of the decomposition of the excited Criegee intermediate (CH<sub>2</sub>OOE, MVKOOA, MACROOA), which can be seen in Fig. 12 and Table 8. The CH<sub>2</sub>OOE intermediate contributes to 0.5 of the excited C.I from the ozonolysis of Isoprene. One of the decomposition routes of the CH<sub>2</sub>OOE intermediate yields an OH and an HO<sub>2</sub> radical from the same channel (MCM predicts 0.27); hence the HO<sub>2</sub> yield for the CH<sub>2</sub>OOE intermediate is equivalent to the

OH yield (0.255±0.022) previously determined. An overall HO<sub>2</sub> yield contribution from CH<sub>2</sub>COOE can be calculated by 0.3×0.255+0.2×0.255=0.127±0.022.

However, the MVKOOA and MACROOA intermediate form OH and HO<sub>2</sub> from distinctly different decomposition channels (Fig. 12) and therefore have their own unique yield (MCM uses 0.255, this study determined 0.263±0.025, using MCM based model fit to HO<sub>2</sub> FAGE data). An overall HO<sub>2</sub> yield contribution from the MVKOOA and MACROOA intermediate can be calculated by 0.3×0.263+0.2×0.263=0.132±0.025.

The overall yield quoted (Table 7) is a combination of these 2 yields which are determined simultaneously using an MCM derived model as previously described; optimising each yield to the OH and HO<sub>2</sub> FAGE data with the assumption that the HO<sub>2</sub> is formed 50% by the CH<sub>2</sub>OOE Criegee intermediate and 50% by the MVKOOA and MACROOA Criegee intermediates (Aschmann and Atkinson, 1994; Grosjean et al., 1993; Jenkin et al., 1997).



**Fig. 12.** Full Isoprene ozonolysis chemistry with MCM based yields.

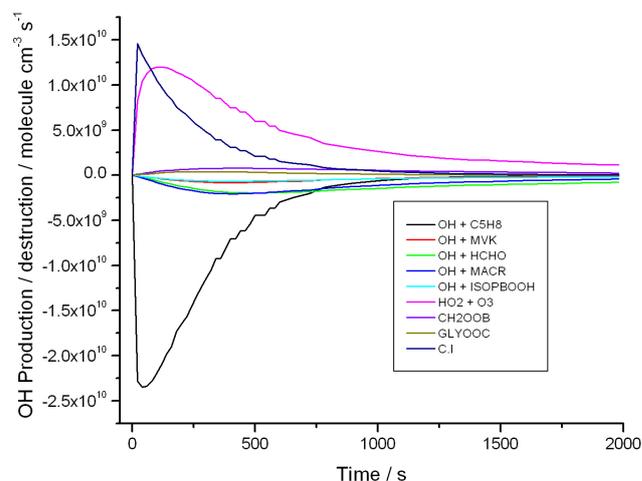
$0.3 \times 0.255$	$=$	$0.0765$
$0.2 \times 0.255$	$=$	$0.0510$
$0.3 \times 0.263$	$=$	$0.0789$
$0.2 \times 0.263$	$=$	$0.0526$
<b>Total</b>		<b>0.259</b>

Following this approach, an overall yield of  $Y_{\text{HO}_2} = 0.127 + 0.132 = 0.259 \pm 0.025$  was determined. The Rate of Production/Destruction Analysis (ROPA/RODA as discussed in Sect. 3.3.1) also classifies these excited Criegee intermediates together.

The processes controlling the production and destruction of OH and HO<sub>2</sub> during the temporal evolution of the experiment are now considered in detail.

### 3.4.1 Model description

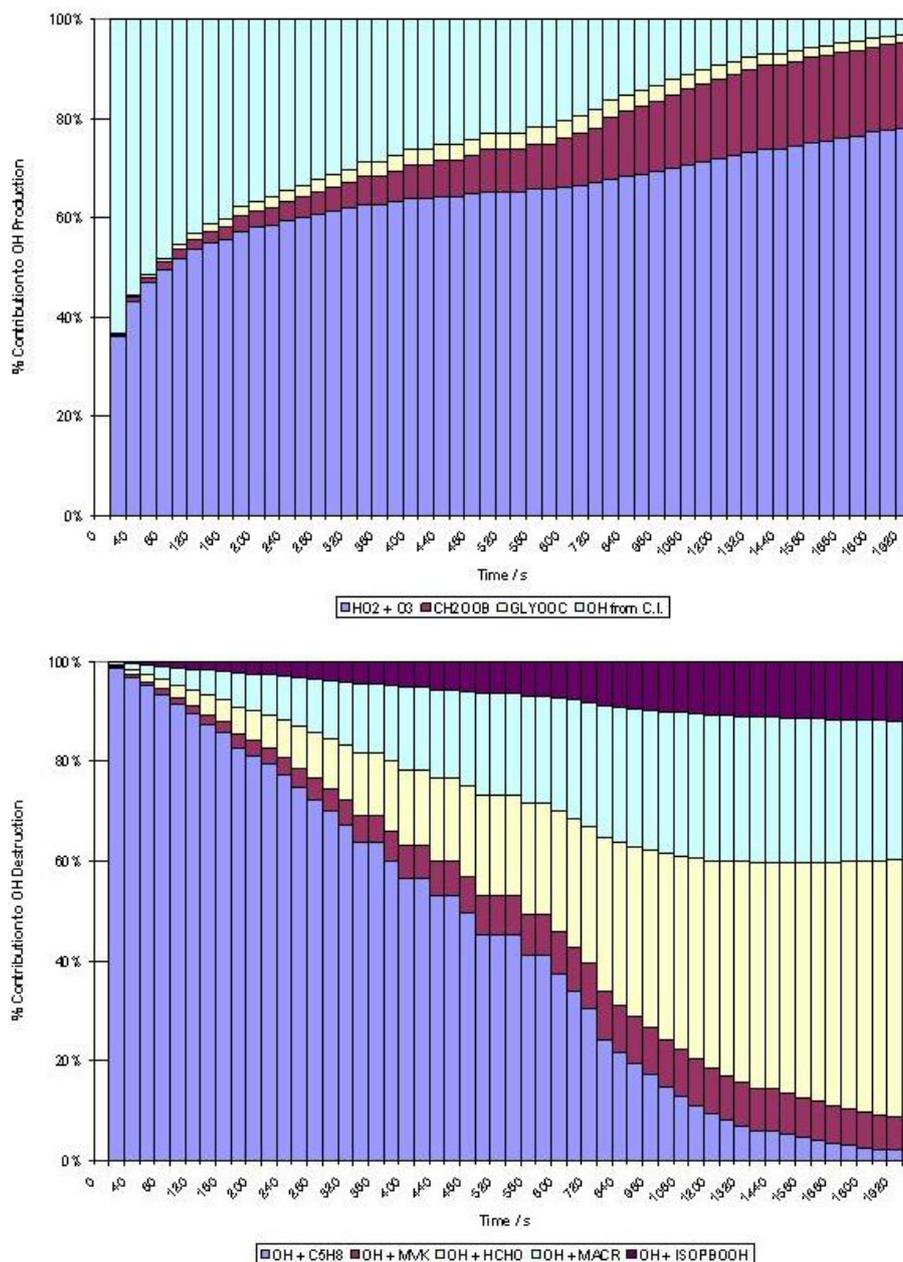
The MCM subset extracted for these simulations included 201 intermediates and 655 reactions. MCM v3.1 specifies that 27% of the Criegee intermediate formed from the O<sub>3</sub>+isoprene reaction yields OH. The OH yield of ozonolysis of isoprene obtained from the data is sensitive to the height and position of the peak OH concentration, as shown in Figures 11a and 11b where the MCM derived model for OH yield=0.27 is compared with yields  $\sim \pm 20\%$  (0.216 and 0.324) and the HO<sub>2</sub> yield=0.263 is compared with yields  $\sim \pm 20\%$  (0.210 and 0.316). This gives support to the derived OH yield from the variable fitting and the data collected and utilised in the model. The temporal profile is very sensitive to



**Fig. 13.** Rate of Production/Destruction Analysis (ROPA/RODA) for OH. The meaning for these abbreviations is given in Table 8.

the OH yield (Fig. 11a and 11b); hence varying the OH yield affects the height and position of the maximum OH concentration. Rate of Production and Destruction Analyses (ROPA and RODA) can be used to gain a better insight into the budget of a given species, in this case the HO<sub>x</sub> radicals, in a particular environment by quantitative analysing the relative importance of different source and sinks.

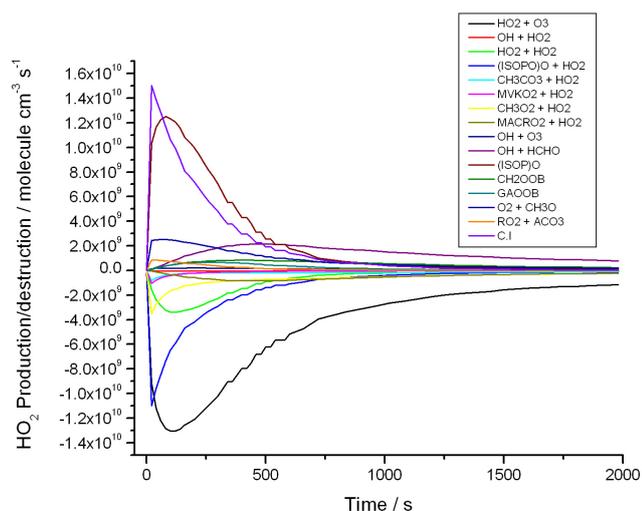
Figures 13 and 14 show the Rate of Production/Destruction Analysis (ROPA/RODA) for OH during the ozonolysis of isoprene (under the previous specified conditions) and identify the main sources of OH production



**Fig. 14.** (a) Percentage contribution of reactions to production of OH. The meaning for these abbreviations is given in Table 8. (b) Percentage contribution of major reactions to the destruction of OH. The meaning for these abbreviations is given in Table 8.

as the decomposition of the Criegee intermediate and reaction of O<sub>3</sub> with HO<sub>2</sub>. OH production by the reaction of O<sub>3</sub> with HO<sub>2</sub> is only a major channel in these direct studies as such a high (~8 ppm) concentration of O<sub>3</sub> is used to drive the reaction of O<sub>3</sub> with isoprene and limit the OH destruction channel of OH reacting with isoprene, hence the concentration of OH in the system is higher and easier to detect. The main destruction pathway for OH is the reaction with isoprene; on longer timescales (>500 s) the main destruction pathway for OH becomes the reaction with

formaldehyde, which is a direct product of the ozonolysis of isoprene. For HO<sub>2</sub> (Figs. 15 and 16), the main sources are the destruction of the Criegee intermediate from isoprene ozonolysis and on longer timescales (>500 s) the main production channel for HO<sub>2</sub> is the reaction of OH and formaldehyde. Unsurprisingly, the main HO<sub>2</sub> destruction channels include the reaction with O<sub>3</sub>, self reaction and the reaction of HO<sub>2</sub> with products from the reaction of OH with isoprene including methyl peroxy radical (CH<sub>3</sub>O<sub>2</sub>).



**Fig. 15.** Rate of Production/Destruction Analysis (ROPA/RODA) for HO<sub>2</sub>. The meaning for these abbreviations is given in Table 8.

#### 4 Discussion

The indirect scavenger, tracer techniques and kinetic study gave the same result within error, with OH yields from the reaction of ozone with isoprene of  $0.25 \pm 0.03$ ,  $0.25 \pm 0.04$  and  $0.27 \pm 0.02$  for TMB as a tracer, cyclohexane as a scavenger and cyclohexane kinetic study respectively (see Table 9). These results are comparable to a majority of the previously published results (Table 1), which use indirect techniques and require some predetermination of factors or assumptions:

- The cyclohexane scavenger technique requires the yield of cyclohexanone product to be determined, in order to obtain the OH yield for the O<sub>3</sub> + isoprene reaction.
- The TMB method requires the stoichiometry of the O<sub>3</sub> + isoprene reaction to be determined to convert the OH yield with respect to ozone to an OH yield with respect to isoprene.

This introduces further errors in to the determined OH yields. The disadvantage to the tracer technique is that each experiment only gives one point and a number of experiments under different conditions are required for one plot (Fig. 6). With the scavenger technique each run gives an OH yield, so an average of many experiments can be taken, reducing the effect of random error. The kinetic study has the complication of only the first 5 points (~250 s) of the reaction being used as on longer timescales (~5 min) products formed in these reactions also react with OH radicals, thus diminishing the consumption of the alkene by reaction (R3). It should be also pointed out that the OH radical yield ( $Y_{OH}$ ) represents an overall yield that also includes a possible contribution from the reaction of the HO<sub>2</sub> radical with O<sub>3</sub>, however with the

**Table 9.** OH Radical Yields in the Gas-Phase Reaction of Ozone with isoprene.

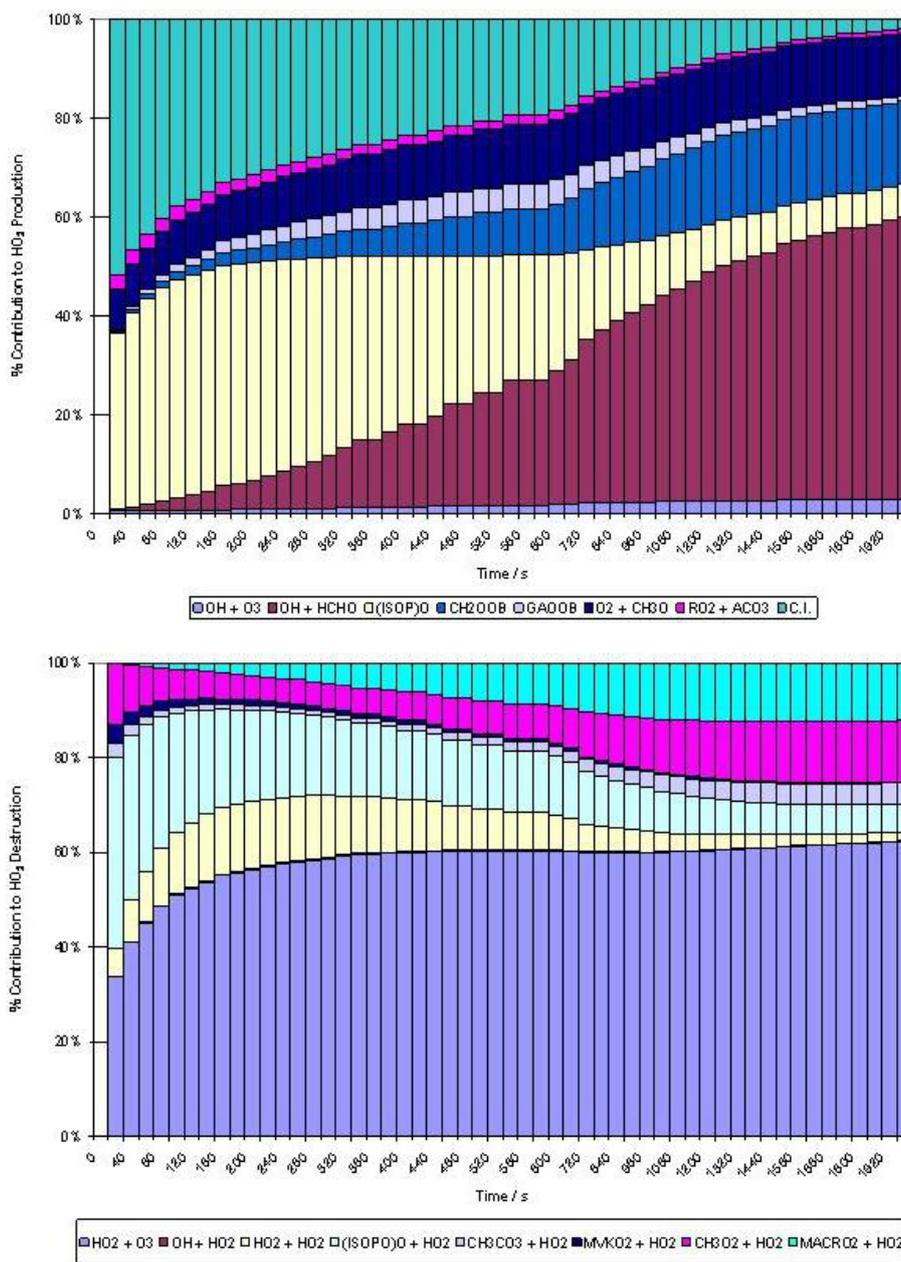
Technique	OH yield
Cyclohexane as a scavenger	$0.25 \pm 0.04$
TMB as a tracer	$0.25 \pm 0.03$
Kinetic study	$0.27 \pm 0.02$
Direct OH detection (FAGE)	$0.26 \pm 0.02$
Recommended <sup>a</sup>	$0.26 \pm 0.02$

<sup>a</sup> Calculated as an average of the 4 methods.

small concentrations of ozone used this is <5%. Direct determination of the OH yield using FAGE has the advantage that the OH yield from the ozonolysis of isoprene is the only variable parameter fitting to the OH data, and that the profile of the OH concentration is very sensitive to the OH yield, hence an accurate determination ( $\pm 10\%$ ) of the OH yield can be obtained.

OH yields obtained in this study for the ozonolysis of isoprene are in good agreement with earlier determinations by Atkinson and co-workers, the more recent results of Paulson and co-workers and Neeb and Moortgat. A set of OH yields that are consistent have now been determined in the current paper using a number of methods: scavenger (cyclohexane), tracer (TMB), kinetic study and direct detection of OH (FAGE). Given the variety of the methods used, and the agreement with many of the previously determined yields, there is now further resolution to the discrepancies seen in the literature.

There remain some discrepancies with the results of Lewin et al. (2001) and Rickard et al. (1999). The reaction stoichiometry calculated by Rickard et al. (1999), ( $1.15 \pm 0.10$ ) is significantly higher than the reaction stoichiometry determined in this study ( $1.00 \pm 0.05$ ). Rickard et al. (1999) observed a correlation between the OH yield and the reaction stoichiometry indicating that the excess consumption of alkene may be linked to the fragment formed as OH is released from the Criegee intermediate. As previously mentioned the formation of OH is thought to result from the decomposition of the Criegee intermediate, with the concomitant formation of a radical of the type CH<sub>2</sub>=CRO<sup>•</sup>. Little is known of the kinetics of these radicals, although it is expected that under conditions of this study they will react with O<sub>2</sub> to generate a peroxy radical of the type <sup>•</sup>O<sub>2</sub>CH<sub>2</sub>CR=O. These radicals are expected to react with other peroxy radicals; however there is limited information is available about the kinetics of these radicals. In principle, the large stoichiometry for the reaction of ozone and isoprene observed in Rickard et al. (1999), could result from the reaction between the peroxy radical and the alkene. However, peroxy radicals generally react slowly with alkenes, having large activation barriers (Rickard et al., 1999). The greater surface-to-volume



**Fig. 16.** (a) Percentage contribution of major reactions to the production of HO<sub>2</sub>. The meaning for these abbreviations is given in Table 8. (b) Percentage contribution of major reactions to the destruction of HO<sub>2</sub>. The meaning for these abbreviations is given in Table 8.

ratio of HIRAC (used in this study) and the reduced concentrations of ozone and isoprene compared to Rickard et al. may account for the difference in the reaction stoichiometry; and possibly the difference in OH yields.

The atmospheric relevance in investigating the OH yield from ozonolysis of isoprene is to support the current recommended OH yield already utilised by the MCM v3.1 (Jenkin et al., 1997, 2003; Saunders et al., 2003) and by IUPAC (Atkinson, 2006). As isoprene is the main biogenic emission (Arneth et al., 2008; Guenther et al., 1995) and as ozonol-

ysis of alkenes can be a predominant source of OH in both urban and rural environments (Emmerson et al., 2007; Lee et al., 2006), it is important for the OH yield to be precisely determined for use in atmospheric models which may affect policy making and protocols.

The first HO<sub>2</sub> yield was directly determined using FAGE. The recommended HO<sub>2</sub> yield from these experiments is  $0.258 \pm 0.025$ . It is important to precisely determine the HO<sub>2</sub> yield due to the HO<sub>x</sub> cycle, also as the HO<sub>2</sub> radical has a concentration of one hundred times the level of OH and a

chemical lifetime of about 100 s (where as OH has a chemical lifetime of about 1 s in the clean troposphere and as low as 10 ms in polluted air), hence contributes to the oxidising capacity of local environment.

## 5 Future Work

The pressure and temperature dependence of the OH yield in the reaction of O<sub>3</sub> + isoprene has not previously been investigated. Some low and atmospheric pressure studies have been published (Table 1); however no agreement on the OH yield pressure profile has yet to be determined. A pressure dependant OH yield profile based on a statistical-dynamical master equation has been calculated by Zhang et al. (2002) discussing the contribution of the prompt and stabilised C.I. channels on the OH yield; it is apparent that there is still much discrepancy in the literature OH yields especially over a wide pressure range. It is important to understand the affect of low pressures on the sensitivity for FAGE, to validate the calibrations and OH concentrations measured on aircraft field campaigns.

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