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Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 1. Ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene

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Abstract. Ozone-alkene reactions generate stabilized Criegee intermediates (of the form R_1R_2COO), which are believed to react with water molecules to form organic hydroperoxides, hydrogen peroxide and carboxylic acids. These reactions are thought to be significant sources of these environmentally important compounds, yet both the yields of stabilized Criegee intermediates and the branching ratios from their reaction with water are not well known. The formation of hydrogen peroxide and organic hydroperoxides was investigated in the gas phase ozonolysis of ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene for relative humidities (RH) from 0 and 80% by gas chromatography with flame ionization detection and high-performance liquid chromatography with fluorescence detection. Additionally, yields of acetaldehyde and acetic acid from *trans*-2-butene and acetone from 2,3-dimethyl-2-butene were measured. The reactions of stabilized Criegee intermediates with water were found to proceed almost entirely via organic hydroperoxide or hydrogen peroxide formation with little acid formation. Stabilized Criegee intermediate yields of 0.39, 0.24, and 0.10 were obtained for ethene, trans-2-butene, and 2,3-dimethyl-2-butene, respectively.

Introduction

The reaction of alkenes with ozone has attracted a great deal of attention in recent years, largely due to its potential environmental impact. Unsaturated hydrocarbons make up about 12% of the total of volatile organic compounds in urban air [*Jeffries*, 1995], and reaction with ozone is a major, and in some cases the dominant, chemical sink for these species, depending on molecular structure and ambient conditions. Under atmospheric conditions, these reactions are believed to produce substantial quantities of hydroxyl radicals [e.g., *Atkinson*, 1997; *Atkinson et al.*, 1992; *Donahue et al.*, 1998; *Mihelcic et al.*, 1999; *Paulson et al.*, 1992, 1999], organic hydroperoxides [*Jackson and Hewitt*, 1999; *Sauer et al.*, 1999; *Winterhalter et al.*, 2000], and organic acids [*Atkinson*, 1997]. Organic hydroperoxide yields of up to 50% [*Neeb et al.*, 1997] have been measured from these reactions. Hydrogen peroxide and organic hydroperoxides have been detected in ambient air and cloud water samples at up to ppb and μmol L^{-1} levels, respectively [e.g., *Gunz and Hoffmann*, 1990; *Jackson and Hewitt*, 1999; *Lee et al.*, 2000]. These compounds are believed to have toxic effects on plants [*Gunz and Hoffmann*, 1990; *Jackson and Hewitt*, 1999; *Lee et al.*, 2000] and have been suggested as a possible source of the toxicity of small (submicron) aerosol particles [*Friedlander and Yeh*, 1998]. Additionally, carboxylic acid yields of up to 50% have been measured from ozone-alkene reactions [*Neeb et al.*, 1997] , although the majority of these species appear to be formed in secondary reactions. Organic acids have been detected in the troposphere both in the gas phase [*Khare et al.*, 1999] and in aerosols [*Saxena and Hildemann*, 1996]. Alkene ozonolysis represents one of just a few known gas phase sources of these compounds [*Pun et al.*, 2000].

Several key aspects of gas phase ozone-alkene reactions are unclear. These uncertainties remain despite the fact that the broad features of the condensed phase mechanism were first proposed over half a century ago [*Criegee*, 1975; *Criegee and Wenner*, 1949]. It is generally accepted that the reaction is initiated with a 1,3 cycloaddition across the double bond to form a primary ozonide (R1), followed by a concerted cycloreversion to produce a carbonyl compound and a so-called Criegee intermediate (hereinafter referred to as CI, (R2)). Based on structural calculations [*Bach et al.*, 1992], the CI is believed to adopt the carbonyl oxide structure shown below, rather than the isomeric dioxirane or *bis*-oxy- forms:

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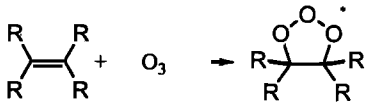
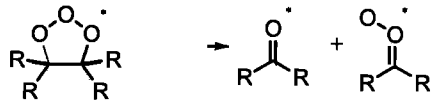
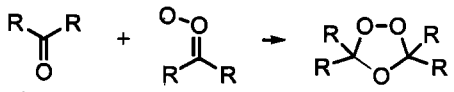
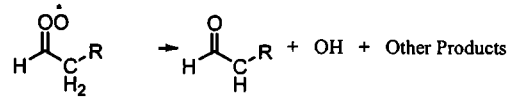
(R1) 

(R2) 

The two fragments produced in reaction (R2) may recombine to form a secondary ozonide (R3). However, reaction (R1) is highly exothermic, resulting in the release of ~60 kcal mol^{-1} into the reaction products [*Gutbrod et al.*, 1996]. Thus a number of unimolecular isomerization and decomposition channels are thermodynamically accessible to the CI (R5), and only a fraction of this species survives long enough to undergo bimolecular reactions. The fraction of the CIs formed that can undergo bimolecular reactions such as (R3) is generally referred to as the stabilized (or thermalized) Criegee intermediate yield (Y_{SCI}) [*Atkinson*, 1997] since the majority of these CIs are either initially formed or collisionally stabilized (R4), such that their internal energy lies below the activation energy of the most facile unimolecular reaction pathway:

(R3) 

(R4)

(R5) 

High yields of OH radicals may be generated in reaction (R5), which subsequently react with the ozonolysis reaction products and the parent alkene. This leads to a greater rate of loss of the alkene relative to that of ozone and renders the determination of the primary product yields from ozone-alkene reactions more difficult.

Very recently, prompt OH radical formation from alkene ozonolysis was investigated by laser-induced fluorescence [*Kroll et al.*, 2001a, 2001b]. From the pressure dependence and temporal behavior of the OH concentrations measured, these researchers concluded that at atmospheric pressure, OH is largely produced from decomposition of the thermalized rather than the internally excited carbonyl oxide. The result that all CIs are completely stabilized under atmospheric conditions is not consistent with yields determined in numerous Criegee scavenger experiments (Table 1), which are typically well below 0.5. Potential reasons for this discrepancy include slow reactions of the scavengers with carbonyl oxides (even with a large excess of scavenger), reaction of dioxiranes with the Criegee scavengers, and stabilization of the vinyl hydroperoxide (produced from the *syn*-carbonyl oxide (R3)) at higher pressures. In addition, *Johnson et al.* [2001] found that excess CI scavengers had no clear effect on OH yields from 2-methyl-2-butene ozonolysis. This implies that OH formation from *syn*-carbonyl oxide is much faster than its bimolecular reactions with Criegee scavengers, which themselves are reasonably close to the collision limit [*Fenske et al.* 2000a]. In the absence of any clear experimental evidence to rationalize the results of *Johnson et al.* [2001] and *Kroll et al.* [2001a, 2001b], we choose not to speculate on the most likely explanation for these observations. In light of these experiments, however, we define the SCI yield as the fraction of CI capable of undergoing bimolecular reactions. We also note that the SCI that we measure is not necessarily the carbonyl oxide, but may have a different form such as dioxirane.

Table 1. SCI Yields from Ozone-Alkene Reactions (Yield Relative to Alkene Reacted With O_3)

Alkene	Reference	Scavenger	Detected Products	Yield
Ethene	This Study	H_2O	HMHP	0.38±0.11
	This Study	HC(O)OH	HPMF	0.39±0.11
	Hatakeyama *et al.* [1994]	SO_2	H_2SO_4	0.39
	Neeb *et al.* [1996]	HC(O)OH	HPMF	0.5
	Horie *et al.*[1999]	$CF_3C(O)CF_3$	-Δ $CF_3C(O)CF_3$	0.52
	Su *et al.* [1980]	CH_2O, CH_3CHO and SO_2	Formic Anhydride, Propene Ozonide and H_2SO_4	0.38[a]
	Kan *et al.* [1981]	CH_2O	Formic Anhydride	0.37[a]
	Niki *et al.* [1981]	CH_2O	Formic Anhydride	0.35[a]
Trans-2-butene	This Study	H_2O	H_2O_2	0.24±0.07
	Hatakeyama *et al.* [1994]	SO_2	H_2SO_4	0.19
	Rickard *et al.* [1999]	SO_2	Δ CH_3CHO	0.13
	Horie and Mootgat [1991]		Computer Simulation	0.42
	Horie *et al.* [1999]	$CF_3C(O)CF_3$	-Δ $CF_3C(O)CF_3$	0.22
2,3-Dimethyl-2-butene	This Study	H_2O	H_2O_2	0.10±0.03
	Niki *et al.* [1987]	H_2CO	Isobutene Ozonide	0.30
	Rickard *et al.* [1999]	SO_2	Δ $(CH_3)_2CO$	0.11
	Horie *et al.* [1999]	$CF_3C(O)CF_3$	-Δ $CF_3C(O)CF_3$	0.29

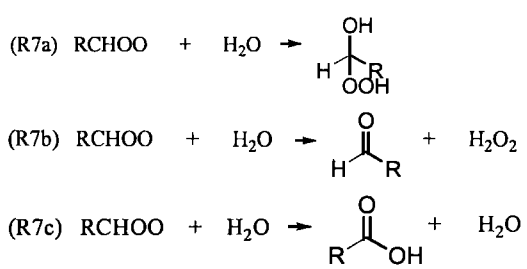
[a] Yield relative to alkene consumed, no OH scavenger

SCIs react with a variety of different compounds, often referred to as Criegee scavengers, including sulfur dioxide [*Hatakeyama and Akimoto*, 1994; *Rickard et al.*, 1999], hexafluoroacetone [*Horie et al.*, 1999], aldehydes, alcohols, carboxylic acids, and water [*Horie and Moortgat*, 1998]. It has also been proposed that CIs react with NO_x [*Atkinson*, 1997]. While the CIs have never been directly observed in the gas phase, their presence has been inferred by detecting the unique products that are formed by their reaction with these compounds. The yield of SCIs has been determined by measuring either the concentration of the unique product or the consumption of the Criegee scavenger in experiments where the scavenger is in "excess". The published data for CI yields are quite scattered. Literature values for this quantity are given in Table 1 for the alkenes of interest.

In the ozonolysis of *trans*-2-butene, secondary ozonide yields of about 20% have been obtained in the presence of approximately 1×10^{15} molecules cm^{-3} acetaldehyde [*Fenske et al.*, 2000a]. In the absence of acetaldehyde, the ozonide yield is considerably lower despite the fact that the stoichiometry of the ozone-alkene reaction is such that enough acetaldehyde is produced to trap all of the SCI. In a recent study in this laboratory, it was shown that these observations could be explained by a unimolecular decomposition channel for the SCI (R6) with a rate coefficient of $80 \pm 30\ s^{-1}$, high enough to be of atmospheric importance [*Fenske et al.*, 2000a]:

(R6) $RCHOO + M \leftrightarrows RCHOO^{*} + M \rightarrow$ products.

In the troposphere, only water, SO_2, and NO_x are likely to be present in sufficient concentrations to react with SCIs. The rate coefficients for these reactions are, however, unknown; estimates span several orders of magnitude. The relative importance of these processes is highly uncertain [*Fenske et al.*, 2000a]. Three channels are thermodynamically accessible for the water reaction, all presumably proceeding through the hydroxyhydroperoxide intermediate):



Very recently, Anglada and coworkers [*Crehuet et al.*, 2001] carried out a theoretical investigation of the $CH_2OO + H_2O$ potential energy surface. Their results indicate that the formaldehyde plus H_2O_2 (R7b), and the formic acid plus water (R7c) reaction channels proceed via the hydroxymethyl hydroperoxide (HMHP) intermediate (R7a) rather than in a one-step reaction. Further, they find that water-catalyzed decomposition of HMHP to H_2O_2 and formaldehyde has a lower activation energy than the corresponding decomposition to formic acid and water (36.7 kcal mol^{-1} and 44.1 kcal mol^{-1}, respectively). Interestingly, Anglada and co-workers [*Crehuet et al.*, 2001] conclude that the most facile decomposition pathway for HMHP is $CH_2(OH)O$-OH bond cleavage to produce OH and, ultimately, HO_2 and formic acid, although our experiments do not confirm this [unpublished work].

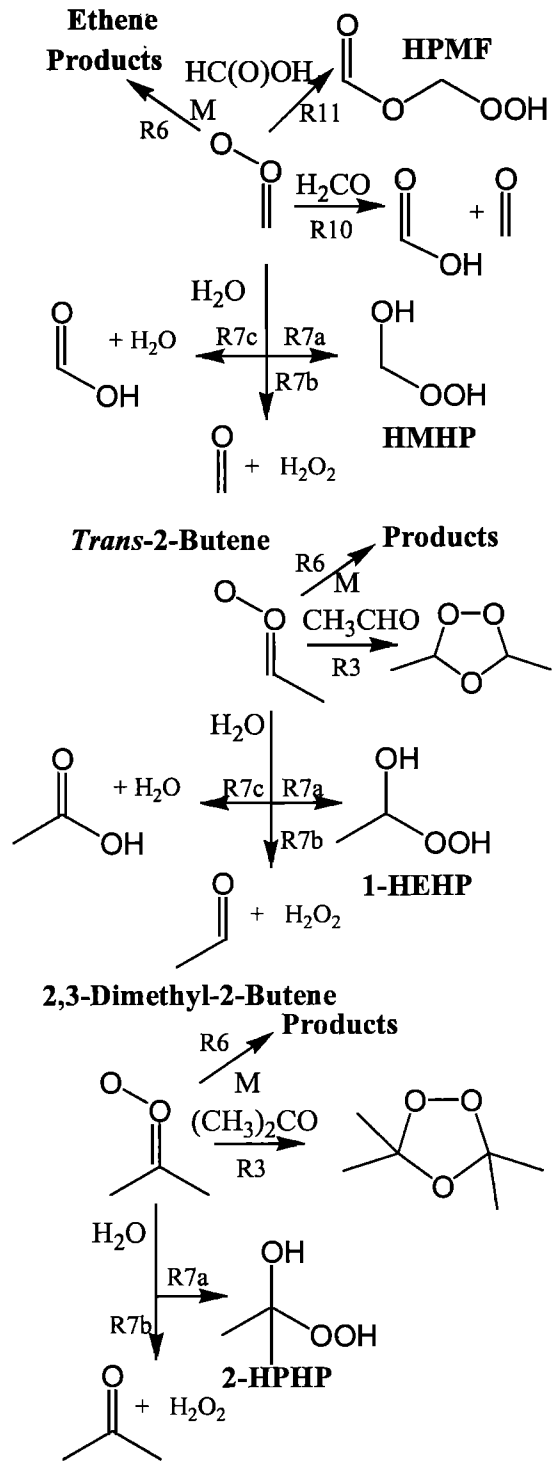


Figure 1. Bimolecular reactions of the Criegee intermediates formed in the ozonolysis of ethene, *trans*-2-butene and 2,3-dimethyl-2-butene.

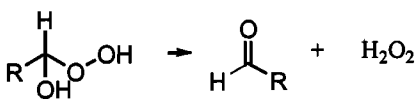
The specific reactions for the SCIs studied here are shown in Figure 1. There is evidence in the literature for all three of these reaction pathways (Table 2); however, quantitative agreement between different studies is generally poor. Additionally, the total yield of products from reaction (R7) is usually much lower than the SCI yield, even under experimental conditions where all of the SCI is expected to react with water. In a series of recent publications, Moortgat

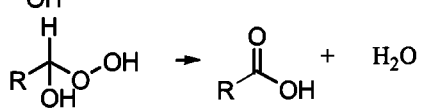
Table 2. Hydroperoxide Yields from Ozone-Alkene Reactions under Dry and Humid Conditions (Yield Relative to Alkene Reacted with O_3 Unless Stated Otherwise)

Alkene	Reference	Detection Method[a]	Hydroperoxide Yield Dry (< 0.5 % RH)	Hydroperoxide Yield Humid (≥ 50 % RH)
Ethene	This Study	HPLC-Fluorescence	Y_{H2O2} = 0.02±0.005 Y_{HMHP} = 0.03±0.01	Y_{H2O2} = 0.05±0.01 Y_{HMHP} = 0.41±0.1
	Neeb *et al.* [1997]	HPLC-Fluorescence	Y_{HMHP} < 0.01	Y_{HMHP} = 0.42
	Gab *et al.* [1995][b]	HPLC-Fluorescence	Y_{H2O2} = 0.004 Y_{HMHP} = 0.002	-
	Hatakeyama *et al.* [1993]	HPLC-Fluorescence	Y_{H2O2} = 0.011 Y_{HMHP} = 0.028	-
	Becker *et al.* [1993]	FTIR/TDLAS	-	Y_{H2O2} = 0.0001
	Hewitt and Kok [1991] [c]	HPLC-Fluorescence	-	Y_{HMHP} = 0.13
	Wolff *et al.* [1997] [c]	HPLC-Fluorescence	Y_{H2O2} = 0.004 Y_{HMHP} = 0.002	-
Trans-2-butene	This Study	HPLC-Fluorescence	$Y_{H2O2+1\text{-}HEHP}$ = 0.08±0.02	$Y_{H2O2+1\text{-}HEHP}$ = 0.32±0.08
	Simonaitis *et al.* [1991]	Fluorescence	-	Y_{H2O2} = 0.16 $Y_{1\text{-}HEHP}$ = 0.2
	Becker *et al.* [1993]	TDLAS	Y_{H2O2} = 0.0006	Y_{H2O2} = 0.005
2,3-Dimethyl-2-butene	This Study	HPLC-Fluorescence	Y_{H2O2} = 0.06±0.02	Y_{H2O2} = 0.16±0.04

[a] TDLAS = Tunable diode laser absorption spectroscopy, FTIR = Fourier transform infrared spectroscopy.
[b] Yield relative to limiting reagent (both alkene and O_3), no OH Scavenger.
[c] Yield Relative to Alkene Consumed, no OH Scavenger.

and coworkers have demonstrated that some hydroxyhydroperoxides formed in reaction (R7a) decompose heterogeneously to form either H_2O_2 and a carbonyl compound (R8a) or water and a carboxylic acid (R8b) [*Neeb et al.*, 1997; *Sauer et al.*, 1999; *Winterhalter et al.*, 2000]:

(R8a)


(R8b)


After correcting for the decomposition of the hydroperoxides, Moortgat and coworkers obtain yields of these compounds that are comparable with SCI yields determined by using different scavengers. They also point out that unless both the rate of decomposition of these compounds and the reaction time are known, the interpretation of hydroperoxide and acid yields is difficult. With the exception of ethene, there have been few measurements of hydroperoxide yields from ozone-alkene reactions. In many of these studies, heterogeneous decomposition of hydroperoxides has been overlooked, and the measured yields are generally much lower than would be expected based on the SCI yields from these reactions.

In this study, hydroperoxide yields have been investigated as a function of water concentration in the ozonolysis of ethene, *trans*-2-butene and 2,3-dimethyl-2-butene. The results provide data on the branching ratios for the three channels of the reaction of SCIs with water (R7) and the yields of SCIs. In contrast to previous investigations, hydroperoxide yields show good agreement with SCI yields measured by other methods, indicating that the data are reliable and that decomposition of hydroperoxide products is not significant. The yields of all observed products can be quantitatively or semiquantitatively explained by self-consistent chemical models, as outlined in our companion paper [*Hasson et al.*, this issue]. The interpretation of the behavior of these simple CIs thus provides a framework for understanding and predicting the chemistry of more complex species.

Experiment

Gas-phase ozone-alkene reactions were performed using a 240-L pillow-shaped Teflon reactor. The reactor was filled with air from a cylinder (Puritan-Bennett, zero grade) or a zero air generator (Thermo Environmental Instruments model 111) adjusted to the required humidity by flowing the air through a water bubbler. Although experiments carried out using dry cylinder air are reported as having been performed at 0% relative humidity (RH), a low concentration (<1% RH) of water, below the detection limit of the hygrometer, may be present owing to desorption from the chamber walls. Appropriate volumes of gas and liquid alkenes were injected into the airflow using a syringe and resulting alkene concentrations were in the range (1.2-2.5) x 10^{14} molecules cm^{-3}. The resultant gas mixture was left in the dark for 1 hour or until the alkene concentration had stabilized. Hydrocarbons, larger carbonyl compounds, and acetic acid were quantified with a gas chromatography with flame ionization detection (GC-

FID) (Hewlett-Packard 5890). Concentrations were calculated using the organic compound's effective carbon number [*Scanlon and Willis*, 1985] and the instrument's carbon response factor, which was remeasured daily using a 4.87 ppm cyclohexane standard (Scott Specialty Gases).

Ozone was generated by passing pure O_2 (ASG, ultra high purity) over a low-pressure mercury penray lamp (Jelight Company). The reaction of ozone with ethene is slow; hence a flow of 0.1 L min^{-1} of the O_3/O_2 mixture was introduced into the reactor for 1 min, and the reaction was monitored by withdrawing samples for GC-FID and high-performance liquid chromatography (HPLC) analysis at 25-min intervals. The remaining ozonolysis reactions are more rapid; hence ozone was added in 30 s, 0.1 L min^{-1} aliquots, and the gas mixture was analyzed once more than 95% of the aliquot of ozone had been consumed. In a typical experiment, a total of about 2.5 x 10^{13} molecules cm^{-3} ozone was added.

The concentrations of hydroperoxides present were determined using a technique relying on the enzyme-catalyzed reaction of hydroperoxides with *para*-hydroxy phenylacetic acid (POHPAA) to produce a dimer, which fluoresces strongly under alkaline conditions. This technique, first described by Gab *et al.* [1985], has been widely used in the analysis of gas phase hydroperoxides in both laboratory and field studies [*Gunz and Hoffmann*, 1990; *Jackson and Hewitt*, 1999]. Gas phase hydroperoxides formed in the reactor were extracted into the aqueous phase using a helical coil collector. The hydroperoxides in the resultant solution were separated by reversed phase HPLC, after which a solution containing POHPAA and the enzyme horseradish peroxidase were added. The concentration of the reaction product was monitored using a fluorescence detector.

The stripping coil was connected to the reactor via unheated ¼-inch Teflon tubing. The coil, based on the design of *Hartkamp and Bachhausen* [1987], consisted of a 1 m x 2 mm internal diameter glass tube containing about 8 turns. The stripping solution, distilled water adjusted to a pH of 1 using phosphoric acid (Fisher, 85 %), was introduced into the coil collector at a flow rate of 0.6 mL min^{-1} using a variable speed peristaltic pump (Rainin Model RP-1). During sampling, gas was withdrawn from the reactor at 3 L min^{-1} for 2 min. The collection efficiency of the coil was found to be ≥92% for samples containing 1 x 10^{13} molecules cm^{-3} of H_2O_2 and peracetic acid ($CH_3C(O)OOH$).

The design of the hydroperoxide detection instrument is shown in Figure 2. The eluent (a 10^{-4} *M* solution of sodium ethylene diamine tetra-acetate, Na_2EDTA, adjusted to a *p*H of 2.5 with sulfuric acid) was delivered at a flow rate of 0.6 mL min^{-1} by an isocratic pump (Shimadzu, LC10-Ai). Samples were introduced into the system through a 20-μL sample loop. Separation of the hydroperoxides was achieved using a 250 mm x 4.6 mm PEEK lined analytical column packed with Inertsil ODS-2 C18 stationary phase (Alltech). At the end of the analytical column, the fluorescence reagent (containing 26 m*M* POHPAA, 0.5 *M* potassium hydrogenphthalate, and 100 units mL^{-1} type II horseradish peroxidase adjusted to a *p*H of 5.8 using sodium hydroxide) was added to the effluent at a rate of 0.06 mL min^{-1} using a peristaltic pump via a PEEK mixing tee. The outlet of the mixing tee was connected to 50 cm of coiled 0.02-inch internal diameter tubing woven in the Serpentine II configuration and thermostatted at 313 K to ensure thorough mixing and the complete reaction of the hydroperoxides with the reagent. The *p*H of the reaction products was raised to ~10.4 by passing the effluent through 5 cm of porous Nafion tubing which was immersed in a vial containing a 28% ammonium hydroxide solution. The outlet of this vial was connected to a commercial fluorescence detector (Shimadzu, RF-10A_{XL}). The concentration of the fluorescent dimer was probed in a 12-μL flow cell using excitation and emission wavelengths of 320 nm and 400 nm, respectively. The signal from the fluorescence detector was recorded and integrated using a PC.

The hydroperoxide signal was calibrated daily using a 9.0 x 10^{-6} *M* H_2O_2 standard solution. Hydroperoxides were identified by comparing their retention times with those of authentic standards. Structures and abbreviations for hydroperoxides are shown in Table 3. Hydroxymethyl hydroperoxide (HMHP), 1-hydroxyethyl hydroperoxide (1-HEHP), methyl hydroperoxide (MHP), performic acid (PFA), and 2-hydroxyethyl hydroperoxide (2-HEHP) are not commercially

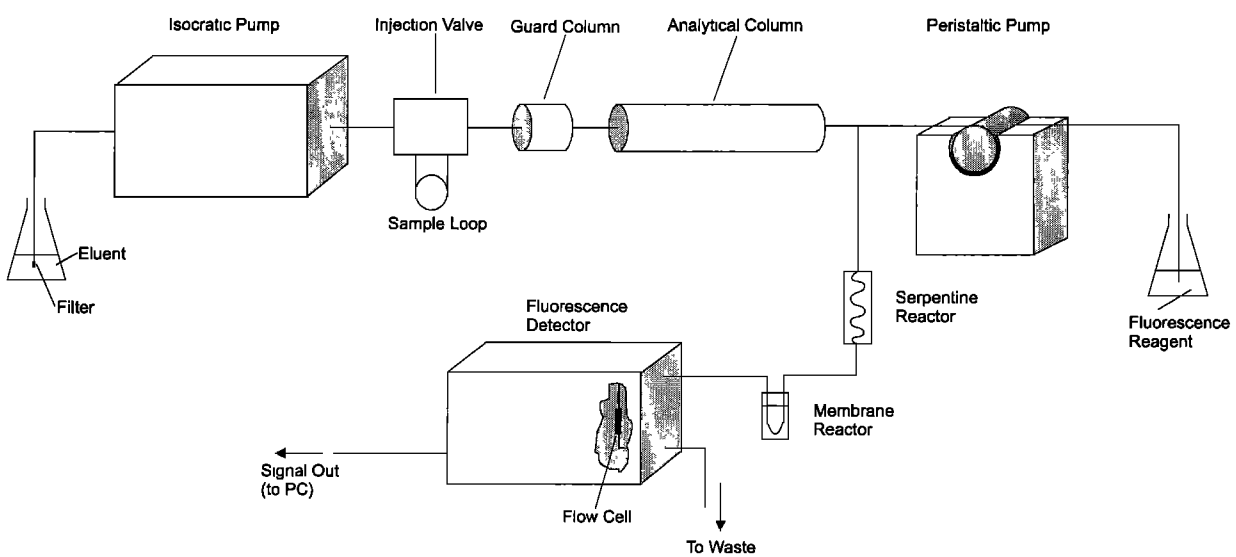
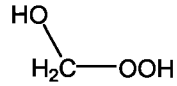
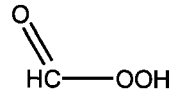
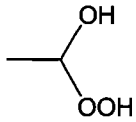
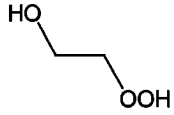
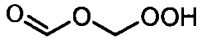
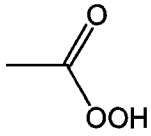
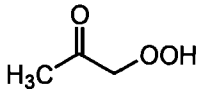


Figure 2. HPLC-Fluorescence apparatus.

Table 3. Structures of the Hydroperoxides Investigated

Peroxide	Formula	Abbreviation
Hydrogen peroxide	H_2O_2	-
Hydroxymethyl hydroperoxide		HMHP
Performic acid		PFA
1-Hydroxyethyl hydroperoxide		1-HEHP
2-Hydroxyethyl hydroperoxide		2-HEHP
Methyl hydroperoxide	CH_3OOH	MHP
Hydroperoxy methyl formate		HPMF
Peracetic acid		PAA
Acetonyl hydroperoxide		AHP

available and were prepared in dilute solution using the methods from the literature [*Greenspan*, 1946; *Kok et al.*, 1995; *Reiche and Hitz*, 1929; *Williams and Mosher*, 1954]. Samples of hydroperoxymethyl formate (HPMF) and acetonyl hydroperoxide (AHP) were prepared in the gas phase by the chlorine atom initiated oxidation of ethylene oxide [*Chen et al.*, 1995] and acetone [*Jenkin et al.*, 1993], respectively.

In all of the experiments, hydroperoxide yields are reported in relation to the amount of alkene reacted with ozone. The ozone-alkene reactions produce OH radicals, and these radicals rapidly add to the parent alkene resulting in a consumption of alkene of greater than one per molecule of ozone reacted. The quantity of alkene reacted with O_3 was therefore calculated by assuming OH yields of 0.18, 0.65, and 1.0 for ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene, respectively [*Paulson et al.*, 1999]. Because of the way that it is reported, product yields for compounds formed by both O_3 and OH reactions may exceed unity. This is the case for acetaldehyde, and acetone from the *trans*-2-butene, and 2,3-dimethyl-2-butene reactions, respectively.

Absolute uncertainties associated with the GC-FID measurements are about ±5%. Since the quantity of ozone-alkene reaction is calculated from the alkene consumption and the OH yield for that ozone-alkene reaction, an additional ±5% error is introduced. Errors in the hydroperoxide concentrations are estimated to be larger (~±25%) because of the possibility of heterogeneous and/or aqueous phase chemistry during the analysis procedure. Combined systematic and random errors associated with the hydroperoxide and carbonyl yields are thus estimated to be ±26% and ±9%, respectively.

Results

Characterization of Peroxide Detection Instrument

In the literature, reported hydroperoxide yields vary dramatically between different studies, despite the use of similar instrumentation and experimental methodologies. These discrepancies probably arise from the difficulties in the quantitative application of the HPLC fluorescence technique to smog chamber experiments. In order to minimize the uncertainties in these experiments, an extensive series of tests was carried out to fully characterize the performance of the peroxide detection instrument.

Hydroperoxides were identified by comparison of their retention times with those of authentic standards. Elution rates were found to be dependent on both the temperature of the column and the *p*H of the eluent; thus retention times were checked whenever these parameters were altered. A peracetic acid standard was run periodically to check for any change in the rate of elution.

Our use of this technique for the quantification of hydroperoxides requires that the response of the instrument is identical for all of the hydroperoxides investigated. This was examined using standardized H_2O_2 and peracetic acid solutions. Figure 3 shows linear response curves for both at the concentrations typical for the chamber experiments, up to 6.75×10^{-5} *M*. The detection limit was found to be about 2×10^{-8} *M*, corresponding to a mixing ratio in the chamber of about 0.1 ppb at 1 atmosphere under typical sampling conditions. The signal response for the two hydroperoxides was found to be experimentally indistinguishable.

Neeb et al. [1997] have demonstrated that the decomposition of hydroperoxides on the walls of reactors and within sampling devices can dramatically affect the measured yields. Thus in order to quantitatively measure hydroperoxide yields, we have characterized these processes. The rate of change of H_2O_2 in our Teflon reactor initially containing 2.3×10^{12} molecules cm^{-3} of this species was described reasonably

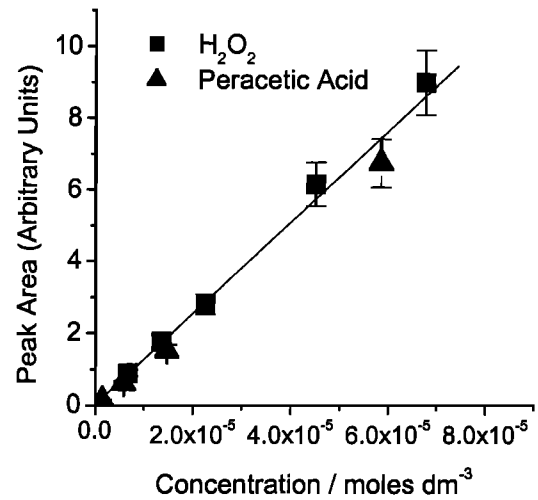


Figure 3. Calibration curve for the fluorescence signal from hydrogen peroxide and peracetic acid.

by first order kinetics with a rate coefficient of 2.0 x 10^{-5} s^{-1}, corresponding to a loss rate of 7 % per hour. In the ozonolysis experiments, the total reaction time was limited to about 2 hours to reduce the potential influence of wall effects. Since the hydroperoxides were generated over the course of the experiments, the average "age" of the hydroperoxides was less than 1 hour. This expected decrease in the hydroperoxide signal during the experiments was masked by the scatter in the data; hence no corrections were applied to the measured hydroperoxide signals. In experiments where the reaction time was longer than 2 hours, the measured hydroperoxide yields were lower than in the shorter-duration experiments, and these data were discarded.

A few experiments to investigate hydroperoxide yields from the ozone-ethene reaction under humid conditions were performed in a 50-L cylindrical Pyrex reactor. In each case, substantially lower HMHP yields, decreasing at longer reaction times, were observed. Larger amounts of formic acid were also observed, although quantitative yields could not be obtained owing to desorption of this compound from the walls of the reactor. Since the difference in surface:volume ratios for the Pyrex and Teflon chambers is too small to explain the different results, these observations coupled to other similar observations in our lab strongly suggest that the rate of decomposition of hydroperoxides is much higher on glass than on Teflon surfaces.

The influence of the coil collector on the measured hydroperoxide yields was investigated by varying the length of the sample line (60 cm to 5 m), the sampling time (30 s to 5 min), the temperature of the coil (273 – 298 K), and the pH of the stripping solution (1-3.5). Only the last of these parameters was found to affect the hydroperoxide distribution, with higher yields of 1-HEHP and hydroperoxy methylformate ($HC(O)OCH_2OOH$, HPMF) obtained under more acidic conditions. Although the partial decomposition of these organic hydroperoxides could not be prevented during sampling and analysis, the gas-phase concentrations could be

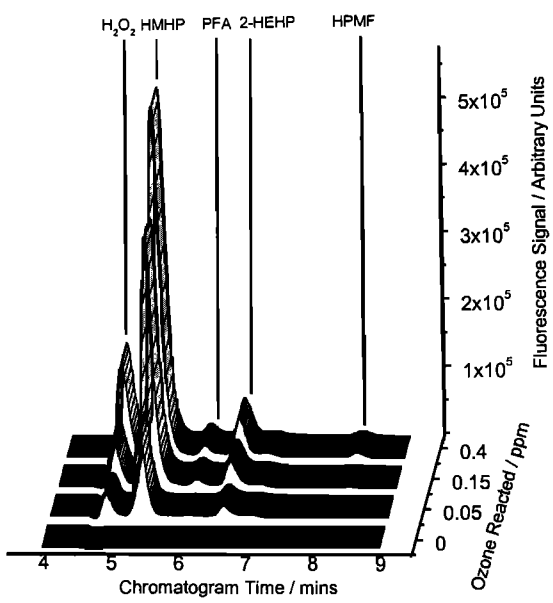


Figure 4. Typical chromatograms from the ozonolysis of ethene at RH = 3.5 %.

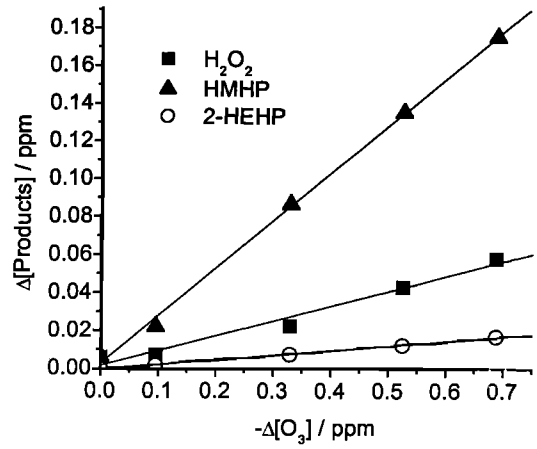


Figure 5. Typical product yield plots from the ozonolysis of ethene at RH = 3.5%.

determined as their decomposition in the aqueous-phase result in the formation of quantifiable hydroperoxide products:

(R9a) R-CH(OH)OOH(aq) → R-CHO(aq) + H_2O_2(aq)
(R9b) $HC(O)OCH_2OOH$(aq) → HC(O)OOH(aq) + H_2CO(aq)

Ethene

The major hydroperoxides detected from ethene ozonolysis in the presence of water vapor are H_2O_2, HMHP, 2-HEHP, and HPMF. The pathways leading to the formation of these species are discussed in detail in section 4; typical chromatograms from an experiment conducted at a relative humidity of 3.5% are shown in Figure 4. Hydroperoxide concentrations were found to increase linearly with the amount of ozone consumed, and their yields (relative to ozone-alkene reaction) were obtained by linear regressions of product yield curves such as those shown in Figure 5.

The dependence of the HMHP and HPMF yields on the water concentration is shown in Figure 6a. In dry air, the yield of HMHP is 0.03. As the relative humidity is increased, the HMHP yield rises rapidly to reach a limiting value of 0.41 at RH ≈ 20%. The hydroperoxide yield then remains unchanged up to RH = 78%, the highest humidity investigated. The yield of HPMF mirrors that of HMHP, dropping from 0.16 at 0% RH to 0 at 78% RH. Yields of 2-HEHP and H_2O_2 (0.05 and 0.03, respectively) were found to be independent of humidity. Two additional experiments were performed in dry air and 2.5 x 10^{14} molecules cm^{-3} of formic acid. The average yields of HMHP and HPMF in the formic acid experiments were 0.005 and 0.39, respectively.

No systematic studies of hydroperoxide yields from ethene ozonolysis as a function of water concentration have been published. However, a substantial number of hydroperoxide yields under "dry" and "humid" conditions have been reported in the literature (Table 2). Under humid conditions, our HMHP yield (0.41) is in excellent agreement with the value reported by *Neeb et al.* [1997] (0.42) but is substantially higher than other reported yields (0.0001-0.13; see Table 2). The most likely cause of the lower values is decomposition of HMHP on the reactor walls. Under dry conditions, our HMHP yield (0.03) is higher than previous measurements, which are typically below 0.01. It is unclear whether the value obtained

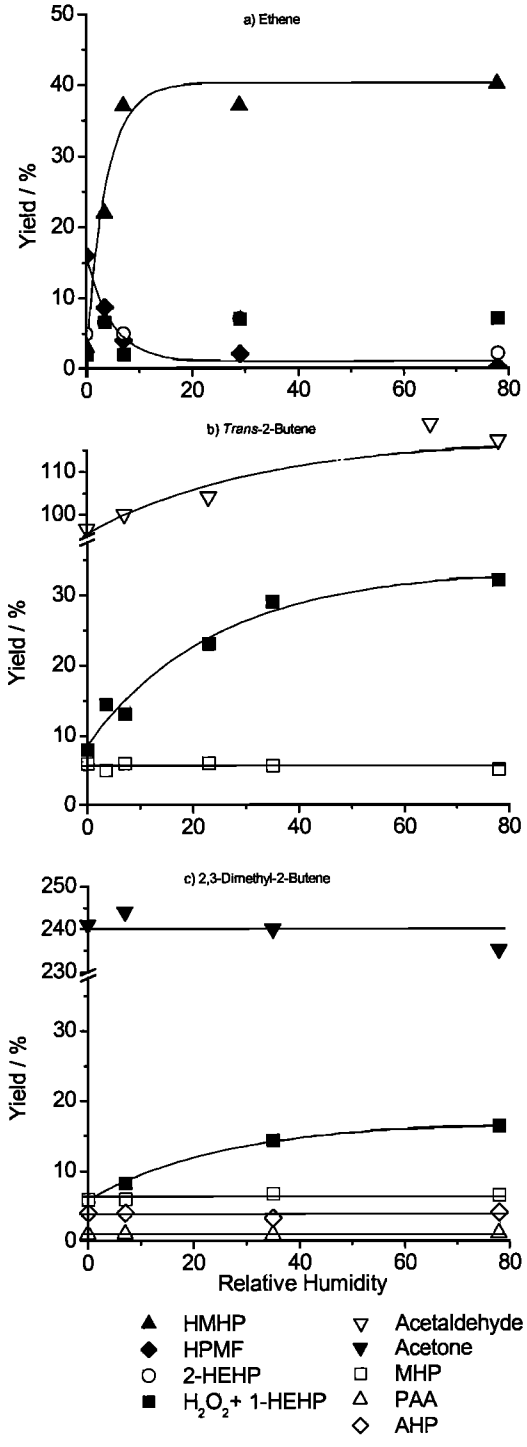


Figure 6. Dependence of the reaction product yields on the relative humidity in the ozonolysis of a) ethene, b) *trans*-2-butene, and c) 2,3-dimethyl-2-butene. Lines are included to guide the eye.

here is higher owing to the lower rate of HMHP decomposition in the Teflon reactor or if it is the result of small quantities of water vapor adsorbed to the walls of the reactor that may desorb when the chamber is filled with dry air. Alternatively, a more complex hydroperoxide formed in the ozonolysis reaction may decompose in the aqueous phase to produce the HMHP observed.

Moortgat and co-workers have measured the yield of HPMF from the ozone-ethene reaction in an excess of formic acid by Fourier transform infrared (FTIR) spectroscopy [*Neeb et al.*, 1996]. In good agreement with our value of 0.39, they report a yield of 0.44, but this value carries with it an uncertainty of about 30%, since they did not have an experimentally determined absorption cross section. *Wolff et al.* [1997] obtained a yield of HPMF of 0.04 under similar conditions but noted that the hydroperoxide was unstable and that this represents a lower limit.

Trans-2-Butene

Substantial yields of H_2O_2, 1-HEHP, and MHP were obtained in the ozonolysis of *trans*-2-butene. In aqueous solution, 1-HEHP was found to decompose completely into acetaldehyde and H_2O_2 in about 30 min. Consequently, a substantial fraction of the 1-HEHP initially present in the sample decomposed in the time required for sampling and HPLC analysis, and the H_2O_2 and 1-HEHP yields could not be independently determined. Thus the sum of the H_2O_2 and 1-HEHP concentrations (hereinafter referred to as H_2O_2 + 1-HEHP) was determined by allowing the 1-HEHP to completely decompose to H_2O_2 before analysis.

The yield of MHP was found to be independent of the relative humidity, with an average yield of 0.06. Yields of H_2O_2 + 1-HEHP as a function of RH are shown in Figure 6b. At 0% RH, the yield of H_2O_2 + 1-HEHP was found to be 0.08. $Y_{H2O2 + 1\text{-}HEHP}$ increases as the humidity rises, reaching its maximum value of 0.32 at 78% RH. $Y_{H2O2 + 1\text{-}HEHP}$ increases more slowly than Y_{HMHP} from ethene and reaches its limiting value at a higher relative humidity (~60%). Experiments performed in the presence of an excess of cyclohexane (to scavenge OH) show that the yield of acetaldehyde is dependent on the relative humidity and follows the same trend as $Y_{H2O2 + 1\text{-}HEHP}$. At 0% RH, the yield is 0.97, rising to a maximum of 1.17 under humid conditions. Under all conditions, a small amount (<0.02) of acetic acid was observed by GC-FID. The acid yields could not be accurately quantified, however, owing to the low signal-to-noise ratio.

Only one previous study of hydroperoxide formation has been published on *trans*-2-butene ozonolysis. *Simonaitis et al.* [1991] measured the yield of H_2O_2 and the sum of organic hydroperoxides at humidities up to 50% (see Table 2). They tentatively assign some of the organic hydroperoxide as 1-HEHP based on its lifetime in aqueous solution compared with that of a 1-HEHP standard. Combining their estimated yield of 1-HEHP with their measured yield of H_2O_2 gives a value for $Y_{H2O2 + 1\text{-}HEHP}$ of 0.36, in good agreement with this work. In contrast to these results, however, they report that the hydroperoxide yields are independent of RH between 5 and 50%. Moortgat and coworkers [*Horie et al.*, 1994] also observed the formation of 1-HEHP in the ozonolysis of *trans*-2-butene under humid conditions, but did not report its yield.

2,3-Dimethyl-2-Butene

Four hydroperoxides were observed in the ozonolysis of 2,3-dimethyl-2-butene: H_2O_2, MHP, PAA, and acetonyl hydroperoxide. The yield of H_2O_2 rises from 0.06 at 0% RH to 0.16 at 78% RH as shown in Figure 6c. The dependence of the H_2O_2 yield on water concentration is similar to that of $Y_{H2O2 + 1\text{-}HEHP}$ from *trans*-2-butene, with Y_{H2O2} reaching its limiting value at ~60% RH. The yields of acetone (2.4), MHP

(0.06), PAA (0.01), and AHP (0.04) are all independent of the relative humidity. To our knowledge, there are no previous measurements of hydroperoxide yields for comparison.

Discussion

The presence of MHP, PAA, 2-HEHP, and AHP as products of these reactions is a result of secondary $RO_2 + HO_2$ reactions [*Hatakeyama et al.*, 1995; *Sauer*, 1997]. Since the focus of this work is the reaction of SCIs, the chemistry of the formation of these species is only briefly discussed. The observation of these hydroperoxides is entirely consistent with the proposed pathways for the unimolecular decomposition of energetically excited CIs. The probable reactions leading to the formation of MHP, PAA, 2-HEHP, and AHP in the ozonolysis of ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene are illustrated in Figure 7. Chemical models including reasonable estimates for the rate coefficients and branching ratios for these reactions were found to agree with the observed product yields to within a factor of 2. The predicted hydroperoxide yields were, however, found to be strongly dependent on the assumed HO_2 yield from alkene ozonolysis. Since this quantity has only been measured for ethene [*Mihelcic et al.*, 1999], detailed results from the modeling study are not presented here.

The observed changes in the yields of H_2O_2 and HMHP at different humidities can be explained by the reaction of SCIs with water (R7). As the concentration of water rises, (R7) competes more effectively with alternate channels such as CI decomposition. The specific reactions leading to hydroperoxide, carbonyl, and acid formation for ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene are shown in Figure 1.

Products From the Stabilized Criegee Intermediate + Water Reaction

In the experiments described here, the hydroxyalkyl hydroperoxide formed in the reaction of water with the SCI (R7a) may decompose in the aqueous phase to H_2O_2 and a carbonyl compound (R9a) following sampling through the coil collector. The direct formation of H_2O_2 and the carbonyl compound in the gas phase reaction of the CI with water (R7b) can, however, be distinguished from the formation of the hydroxyalkyl hydroperoxide in the gas phase followed by its aqueous phase decomposition (reaction (R7a) followed by (R9a)) because in the former case, the gas phase yield of the compound R-CHO changes as a function of relative humidity. In the latter case, the carbonyl yield (which is measured by GC-FID) should be independent of RH except in the unlikely event that hydroxyalkyl hydroperoxides decompose to carbonyls and H_2O_2 in the GC column. There is evidence suggesting that this is not the case, including good agreement between carbonyl yields from ozone-alkene experiments at high RH measured by GC-FID and FTIR [*Atkinson*, 1997; *Winterhalter et al.*, 2000], and the recent observation of HMHP by gas chromatography-mass spectrometry (GC-MS) in this laboratory [Unpublished work].

In the ozonolysis of ethene, the yield of HMHP from the reaction of SCI with water (R7a) rises rapidly as the humidity increases. The yield of H_2O_2 is low and independent of the relative humidity, implying that the channel of the SCI-water reaction leading to the formation of H_2O_2 and formaldehyde

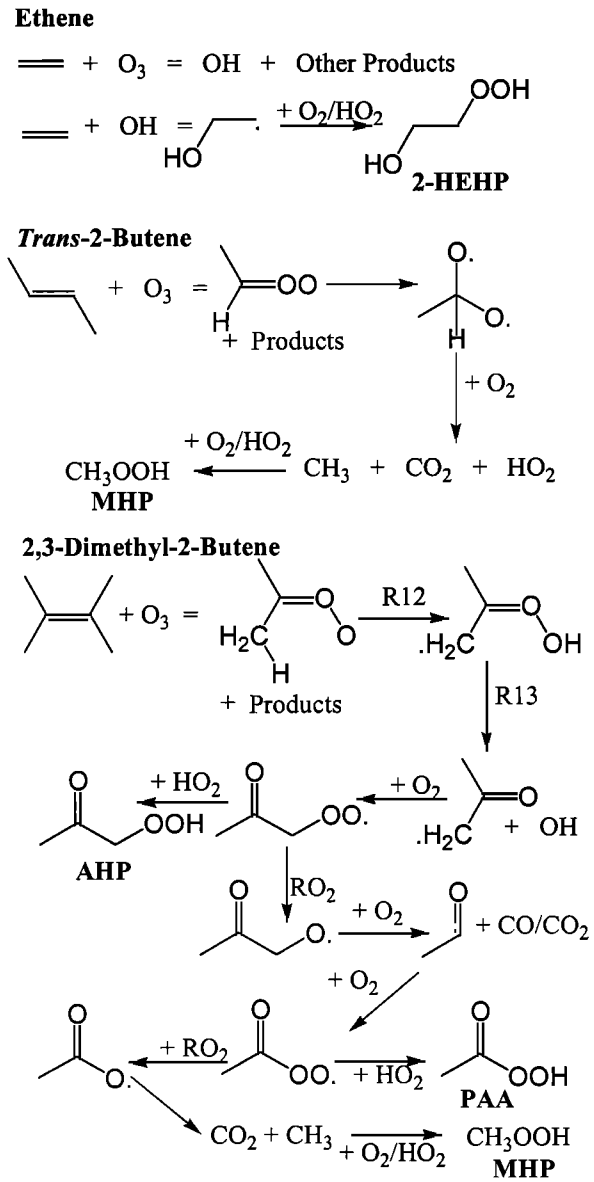


Figure 7. Pathways leading to the formation of observed hydroperoxides via $RO_2 + HO_2$ reactions in the ozonolysis of ethene, *trans*-2-butene and 2,3-dimethyl-2-butene.

(R7b) is negligible. On the other hand, the presence of HPMF can be explained by the reactions

(R10) $H_2COO + H_2CO \rightarrow HC(O)OH + H_2CO$
(R11) $H_2COO + HC(O)OH \rightarrow HC(O)OCH_2OOH$

The high-pressure limit of the rate coefficient for SCI plus formic acid (R11) is approximately 10^4 higher than the rate coefficient for the reaction of SCI with water (R7) [*Neeb et al.*, 1996]. Thus if a significant amount of formic acid is produced via (R7), formic acid would still be able to compete with water at high RH. The HPMF yield of about zero at RH greater than 10 implies that formic acid production from (R7c) is low and that CH_2OO reacts with water to produce only HMHP (*via* reaction R7a). Further, low formic acid yields at high RH along with H_2O_2 and 2-HEHP yields that are invariant with changing humidity imply that the

decomposition of HMHP to OH, HO_2, and formic acid as proposed by *Crehuet et al.* [2001] is not significant.

In the case of *trans*-2-butene, the yield of 1-HEHP + H_2O_2 increases substantially, from 0.08 to 0.32, increasing RH as the water reaction becomes the only CI sink. This rise could be the result of the formation of 1-HEHP in the reaction of CH_3CHOO with water followed by the decomposition of the hydroperoxide to H_2O_2 and acetaldehyde ((R7a plus (R9a)), the direct formation of acetaldehyde and hydrogen peroxide from the reaction of SCI with water (R7b), or a combination of both channels. The yield of acetaldehyde increases by 0.20 in the presence of water vapor, indicating that the major channel in the CI-water reaction produces acetaldehyde and H_2O_2 directly (R7b), and that the production of 1-HEHP (R7a) is a much less significant reaction. Under all conditions, the yield of acetic acid was less than 0.02 implying that its formation in the reaction of water with CH_3CHOO (R7c) is a minor pathway.

In the ozonolysis of 2,3-dimethyl-2-butene, only the yield of H_2O_2 increases with relative humidity. The corresponding hydroxyalkylhydroperoxide from the reaction of water with $(CH_3)_2COO$ (R7a), hydroxypropyl hydroperoxide (2-HPHP), is not detected; however, a portion of the observed H_2O_2 could be produced via the aqueous phase decomposition of 2-HPHP ((R7a) followed by (R9a)). No increase in the yield of acetone was apparent as the humidity rose, which nominally implies that H_2O_2 is not formed directly by the reaction of SCI with water. However, the acetone yield under dry conditions is about 2.4. Given a SCI yield of 0.1 (see below), even if the $(CH_3)_2COO$ reaction with water proceeded entirely by pathway (R7b) to form acetone and H_2O_2, the acetone yield would only increase to 2.5 under humid conditions. This represents only a 4% change, lower than the experimental uncertainty. Thus it was not possible to distinguish between the organic hydroperoxide and the H_2O_2/acetone forming channels of the $(CH_3)_2COO$ reaction with water ((R7a) and (R7b), respectively). For this CI, the carboxylic acid-forming channel (R7c) is not possible, since there are no α-H atoms available to undergo this rearrangement.

In summary, the estimated branching ratios for the reactions of CH_2OO with water are >0.9, 0, and <0.1 for HMHP (R7a), formaldehyde/H_2O_2 (R7b), and formic acid/H_2O (R7c), respectively. For CH_3CHOO, the estimated branching ratios are 0.15, 0.77, and 0.08 for (R7a), (R7b), and (R7c), respectively (as determined from the relative yields of H_2O_2 + 1-HEHP, acetaldehyde, and acetic acid). In previous studies, the reaction of water with SCIs (R7c) was believed to be the source of carboxylic acids in ozone-alkene reactions under humid conditions. More recently, Moortgat and coworkers demonstrated that the temporal behavior of formic acid in ethene ozonolysis is consistent with the formation of HCO_2H as a secondary product from heterogeneous HMHP decomposition (R8b) [*Neeb et al.*, 1997]. However, they were unable to prevent this decomposition process, hence their conclusions were equivocal. Here, by measuring the primary product yields from the SCI reaction with water, their assertion that carboxylic acid formation is a minor pathway from this process is shown to be correct.

Kinetics of Stabilized Criegee Intermediate Reactions

In Figure 6, it can be seen that the yield of HMHP from ethene ozonolysis increases as the humidity increases, asymptotically approaching a maximum value. The same behavior is observed for 1-HEHP/H_2O_2 and H_2O_2 formation in the reactions of ozone with *trans*-2-butene and 2,3-dimethyl-2-butene, respectively. SCIs are known to react with the carbonyl compounds cogenerated with the CIs in the first stage of ozone-alkene reactions (R3), and CH_2OO reacts with formic acid (above). Recent theoretical and experimental work has indicated that thermal decomposition of the SCI may also be important [*Fenske et al.*, 2000a; *Olzmann et al.*, 1997] (R6). In the absence of water vapor, SCIs react via both reaction with carbonyl compounds or acids (R3) and unimolecular decomposition (R6). As the concentration of water increases, the water reaction with SCIs (R7) becomes increasingly competitive. Plots of hydroperoxide yields as a function of RH (such as Figure 6) therefore contain information regarding the relative rates of the SCI reactions. Since there are so few measurements of these processes in the literature, and no complete set for any one CI, however, it is not possible to evaluate in detail the relative importance of these three reactions in determining the observed experimental behavior. Qualitatively, however, the observation that hydroperoxide yields reach a maximum at lower RH for ethene than for trans-2-butene or 2,3-dimethyl-2-butene is consistent with theoretical results that decomposition is slower for CH_2OO than for larger CIs.

Stabilized Criegee Intermediate Yields

Having shown that the organic hydroperoxide (R7a) and H_2O_2/carbonyl compound (R7b) channels account for virtually all of the products of the SCI reaction with water, the hydroperoxide yields can be used to determine the SCI yields for the three alkenes discussed here. Assuming that no other channels have been overlooked for the reaction of the SCI with water, Y_{SCI} is simply given by the increase in the hydroperoxide yield from 0% to 78% RH (provided the hydroperoxide yield has reached its maximum at 78% RH). This assumes that all of the H_2O_2 and organic hydroperoxides that are observed in the 0% RH experiments originate from HO_2-RO_2 and RO_2-RO_2 reactions (see Figure 7). However, as mentioned previously, in the 0% RH experiments, some water may still be present as a result of desorption from the chamber walls. Although the effects of this water vapor are expected to be small, a slight systematic underprediction of the SCI yield cannot be completely excluded. HPMF yields from ethene-ozone reactions performed in excess formic acid provide additional data on Y_{SCI} for this alkene. The values obtained for ethene, *trans*-2-butene, and 2,3-dimethyl-2-butene are 0.39, 0.24, and 0.10, respectively (Table 1). These yields are in good agreement with previous measurements, although the yield for 2,3-dimethyl-2-butene lies at the lower end of the range (Table 1). As well as providing data on SCI yields, these values represent an important crosscheck of the accuracy of the hydroperoxide yields measured here. Thus these SCI yields instill confidence that the trends observed in the hydroperoxide yields reflect the underlying chemistry rather than experimental uncertainties.

It is interesting to note that the yields of SCIs from alkene ozonolysis increase in the order 2,3-dimethyl-2-butene < *trans*-2-butene < ethene; the reverse of the order of OH yields ethene < *trans*-2-butene < 2,3-dimethyl-2-butene. Previous evaluations of literature data have established a weak anticorrelation between OH yield and SCI yield [*Paulson et al.*, 1999; *Rickard et al.*, 1999]. The relationship between these two important products is discussed in detail in our companion paper [*Hasson et al.*, this issue].

Conclusions

The experimental data presented here are consistent with three competitive reaction channels for the CI: reaction with water, reaction with carbonyls and acids, and unimolecular decomposition. Under atmospheric conditions, carbonyl and acids concentrations are too low for them to be a significant sink for SCIs. The possible fates of SCIs are thus decomposition, reaction with water, SO_2, and possibly NO_x. For CH_2OO, decomposition is negligible, but for larger CIs this may be a significant sink depending on the ambient humidity, NO_x, and SO_2 concentrations. The reaction of CH_2OO with water produces HMHP in high yield while the corresponding reactions of CH_3CHOO and $(CH_3)_2COO$ predominantly generate H_2O_2 and acetaldehyde or acetone, respectively. Organic acid formation represents a minor pathway.

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