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Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 2. Asymmetric and biogenic alkenes

Alam S. Hasson [1]

Department of Atmospheric Sciences, University of California at Los Angeles, Los Angeles, California, USA

Andy W. Ho[2], Keith T. Kuwata[3]

Department of Chemistry, University of California at Los Angeles, Los Angeles, California, USA

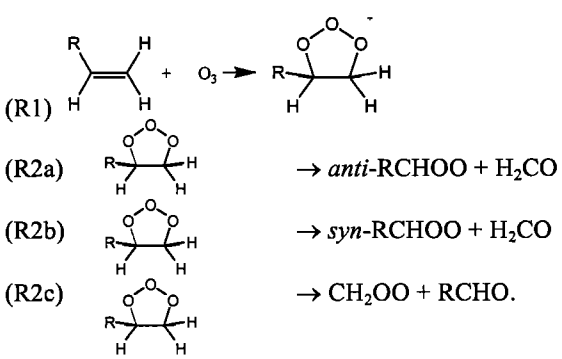
Suzanne E. Paulson

Department of Atmospheric Sciences, University of California at Los Angeles, Los Angeles, California, USA

Abstract. Organic hydroperoxide, hydrogen peroxide, and $>C_1$ carbonyl yields have been measured from the reaction of a set of structurally diverse and atmospherically significant terminal and exocyclic alkenes with ozone. Product yields were investigated for 1-butene, 1-pentene, 1-octene, methylene cyclohexane, β-pinene, camphene and isoprene for humidities from 0 to 80% using gas chromatography with flame ionization detection and high-performance liquid chromatography with fluorescence detection. The yields of these products were used to estimate the following stabilized Criegee intermediate yields: 1-butene (0.27), 1-pentene (0.29), 1-octene (0.36), methylene cyclohexane (0.18), β-pinene (0.28), camphene (0.31), and isoprene (0.27). The reaction of stabilized Criegee intermediates with water produces primarily hydroxymethyl hydroperoxide from CH_2OO, and H_2O_2 and a carbonyl compound for larger Criegee intermediates; acid formation is expected to be low. The exception is camphene, for which the large Criegee intermediate generates the corresponding hydroxyalkyl hydroperoxide in its reaction with water. These results were used to develop a structure activity relationship to estimate stabilized Criegee intermediate yields and to demonstrate that this model is consistent with literature values for OH yields from these ozone-alkene reactions. The mechanisms of the formation of these products are discussed and a hypothesis for the decrease in OH formation with increasing chain length for terminal alkenes is provided. Finally, a parameterization of the reactions for incorporation into atmospheric models is developed.

Introduction

Gas phase ozonolysis is potentially a major sink for unsaturated hydrocarbons in the atmosphere. Recent modeling calculations indicate that under certain atmospheric conditions, these reactions may be the dominant source of tropospheric HO_x and hydroperoxides [*Ariya et al.*, 2000; *Paulson and Orlando*, 1996]. A sound understanding of the mechanisms of these reactions is thus crucial for the development of accurate photochemical models. However, despite numerous recent studies of OH yields from ozone-alkene reactions [e.g., *Atkinson*, 1997; *Paulson et al.*, 1999], both hydroperoxide yields and the mechanisms of their formation remain uncertain. In the first stage of the reaction, ozone adds across the double bond to produce a primary ozonide (R1), which rapidly undergoes a cycloreversion reaction (R2) to give a carbonyl compound and a so-called Criegee intermediate (CI) [*Criegee*, 1975; *Criegee and Wenner*, 1949]. Calculations presented here indicate that the formation of RCHO and CH_2OO (R2c) actually proceeds via two distinct transition states with different activation energies, thus both of these pathways must be considered when determining the branching ratios of the cycloreversion reactions (section 4.3):



[1] Now at Department of Chemistry, California State University, Fresno, California, USA.

[2] Now at Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, USA.

[3] Now at Department of Chemistry, Macalester College, St. Paul, Minnesota, USA.

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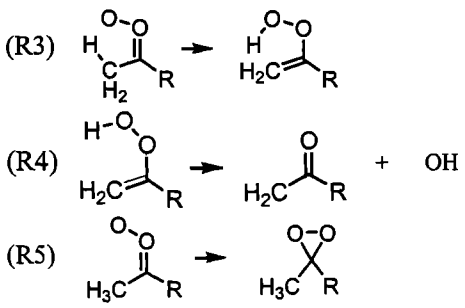
Although never directly observed in the gas phase, electronic structure calculations [*Bach et al.*, 1992] and circumstantial experimental evidence indicates that the structure of these molecules is that of the carbonyl oxide (gas phase CI chemistry closely resembles that of condensed phase carbonyl oxides [*Adam et al.*, 1989]). The fate of these intermediates is highly uncertain, and it is the difficulty in characterizing the reactions of these species that is the origin of the uncertainties in the gas phase ozonolysis reaction mechanisms.

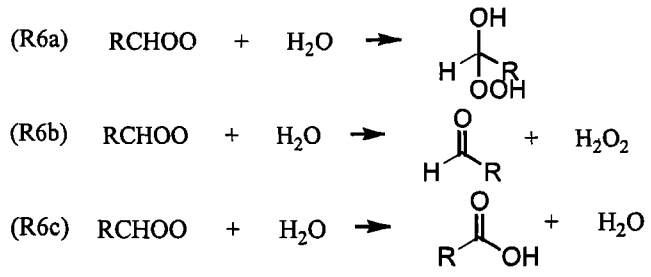
The ozone-alkene reaction is highly exothermic, resulting in the release of about 60 kcal mol^{-1} into the reaction products [*Gutbrod et al.*, 1996]. As a consequence of this, a significant proportion of the CI is initially produced with excess internal energy. A number of unimolecular isomerization and decomposition channels are thermodynamically accessible to these molecules. Theoretical studies indicate that for *syn*-carbonyl oxides, the most facile reaction is isomerization to a vinyl hydroperoxide (R3) with isomerization to a dioxirane (R5) as the second most favorable pathway [*Olzmann et al.*, 1997]. For *anti*-carbonyl oxides, (R3) cannot occur, and so dioxirane formation is the lowest-energy pathway:



Reaction (R3) is believed to result in the formation of OH radicals via cleavage of the O-O bond (R4).

A significant fraction of the CIs produced when the primary ozonide decomposes (R2) survive to undergo secondary reactions [*Atkinson*, 1997]. These species are either generated with insufficient internal energy to surmount the barriers for unimolecular reactions, or they are stabilized via collisional energy transfer before these reactions can occur. Such molecules are referred to as stabilized (or thermalized) Criegee intermediates (hereinafter referred to as SCI). SCIs are believed to react with a variety of different compounds (so-called Criegee scavengers) such as sulfur dioxide [*Hatakeyama and Akimoto*, 1994], NO_x [*Atkinson*, 1997], hexafluoroacetone [*Horie et al.*, 1999], aldehydes, alcohols, carboxylic acids and water [*Horie and Moortgat*, 1998]. The yields of SCIs have been estimated by measuring the product yields of their reactions with an excess of Criegee scavenger.

In the atmosphere, only SO_2, NO_x, and water are likely present in sufficient concentrations to potentially provide effective chemical sinks for SCIs [*Fenske et al.*, 2000a]. The reaction with water is believed to proceed via three channels leading to the formation of organic hydroperoxides (R6a), H_2O_2 (R6b), and carboxylic acids (R6c); hydroperoxides relevant to this study are listed in Table 1.



Quantifying the formation of these products is important for a complete evaluation of the environmental impact of unsaturated compounds since these species have been implicated in important issues such as environmental health [*Friedlander and Yeh*, 1998] and particle formation [*Saxena and Hildemann*, 1996].

Relatively few SCI and hydroperoxide yields have been published for the compounds investigated in this study. A number of researchers have reported H_2O_2 yields for isoprene ozonolysis under dry and humid conditions (Table 2), but the data are highly scattered. Moortgat and coworkers have also reported yields of H_2O_2 from the β-pinene-ozone reaction as a function of relative humidity [*Winterhalter et al.*, 2000]. SCI yields have also been published for 1-octene [*Paulson and Seinfeld*, 1992], isoprene [*Rickard et al.*, 1999], β-pinene [*Hatakeyama and Akimoto*, 1994], and methylene cyclo hexane [*Hatakeyama and Akimoto*, 1994]. As far as we are aware, there are no literature values for SCI yields from 1-butene, 1-pentene, and camphene or for hydroperoxide yields from 1-butene, 1-pentene, 1-octene, camphene, and methylene cyclohexane. In this study, hydroperoxide formation from the reaction of water with SCIs from 1-butene, 1-pentene, 1-octene, isoprene, β-pinene, camphene and methylene cyclohexane has been investigated. The data from these experiments provide information on the mechanisms of ozonolysis reactions and on the fate of these atmospherically important compounds. These experiments thus provide a reasonably large, self-consistent data set for the development of protocols to predict hydroperoxide and SCIs from ozone-alkene reactions and to explain the relationship between OH yields and SCI yields. These models are entirely consistent both with the accepted mechanisms of gas phase ozonolysis of alkenes, and with literature values for these quantities.

Table 1. Structures of the Hydroperoxides Investigated

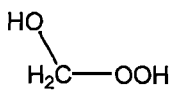
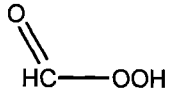
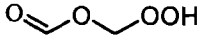
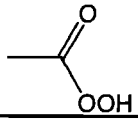
Peroxide	Formula	Abbreviation
Hydrogen peroxide	H_2O_2	
Hydroxymethyl hydroperoxide		HMHP
Performic acid		PFA
Methyl hydroperoxide	CH_3OOH	MHP
Hydroperoxy methyl formate		HPMF
Peracetic acid		PAA

Table 2. Product Yields from Ozone-Alkene Reactions (Relative to Alkene Reacting with O_3 unless Stated Otherwise)

Alkene	Reference	Product Yield		
1-Butene	This Study		Dry[a]	Humid[b]
		Y_{HMHP} =	0.007±0.002	0.15±0.04
		Y_{H2O2} =	0.013±0.003	0.11±0.03
		$Y_{Propanal}$ =	0.36±0.03	0.52±0.05
	Becker et al. [1993]	Y_{H2O2} =		0
	Hewitt and Kok [1991][c]			In Presence of Bulk Water
		Y_{HMHP} =		0
		Y_{H2O2} =		0.18
	Grosjean et al. [1996a]	$Y_{Propanal}$ =	0.35	
1-Pentene	This Study	Y_{HMHP} =	0.006±0.002	0.13±0.03
		Y_{H2O2} =	0.014±0.004	0.16±0.04
		$Y_{Butanal}$ =	0.38±0.03	0.55±0.05
	Wolff et al. [*1996*][c]	Y_{HMHP} =		0.025
		Y_{H2O2} =		0.028
	Atkinson et al. [1995]		RH = 3-7%	
		$Y_{Butanal}$ =	0.541	
	Grosjean and Grosjean [1996]	$Y_{Butanal}$ =		0.496
1-Octene	This Study	Y_{HMHP} =	0.003±0.001	0.12±0.03
		Y_{H2O2} =	0.021±0.005	0.20±0.05
		$Y_{Heptanal}$ =	0.38±0.03	0.66±0.06
	Atkinson et al. [1995]		RH = 3-7%	
		$Y_{Heptanal}$ =	0.452	
	Grosjean et al. [1996b]	$Y_{Heptanal}$ =		0.473
Methylene Cyclohexane	This Study	Y_{HMHP} =	0.005±0.001	0.03±0.01
		Y_{H2O2} =	0.035±0.009	0.12±0.03
		Y_{ketone} =	0.19±0.01	0.33±0.03
	Hatakeyama et al. [1993]			RH = 10-17%
		Y_{HMHP} =	0.0044	0.03
		Y_{H2O2} =	0.0047	0.013
β-Pinene	This Study	Y_{HMHP} =	0.001±3x10^{-4}	0.02±0.005
		Y_{H2O2} =	0.03±0.01	0.25±0.07
		$Y_{Nopinone}$ =	0.26±0.01	0.53±0.05
	Gab et al. [1995]	Y_{H2O2} =	0.006	
	Becker et al. [1993]	Y_{H2O2} =		0.0015
	Hewitt and Kok [1991][c]			In Presence of Bulk Water
		Y_{H2O2} =		0.17
	Simonaitis et al. [1991]			RH = 42%
		Y_{H2O2} =		0.17
	Winterhalter et al. [2000]	Y_{H2O2} =	0.002	0.24
		$Y_{Nopinone}$ =	0.16	0.52
	Grosjean et al. [1993b]	$Y_{Nopinone}$ =		0.22
	Hakola et al. [1994]		RH = 3-7%	
		$Y_{Nopinone}$ =	0.23	
	Rickard et al. [1999]		Dry	
		$Y_{Nopinone}$ =	0.23	
Camphene	This Study	Y_{HMHP} =	0.02±0.005	0.15±0.04
		Y_{H2O2} =	0.14±0.04	0.31±0.08
		$Y_{Camphenulone}$ =	0.42±0.04	0.46±0.04
	Hakola et al. [1994]		RH = 3-7%	
		Y_{ketone} =	0.36	
	This Study	Y_{HMHP} =	0.01±0.003	0.16±0.04
		Y_{H2O2} =	0.05±0.01	0.12±0.03
		Y_{MAC} =	0.35±0.03	0.42±0.04
		Y_{MVK} =	0.17±0.02	0.24±0.02
	Neeb et al. [1997] *Sauer et al.* [1999]	Y_{HMHP} =	0.01	0.30
		Y_{H2O2} =	0.01	0.09
		Y_{MAC} =	0.35[c]	0.40[c]
		Y_{MVK} =	0.14[c]	0.20[c]
	Simonaitis et al. [1991]	Y_{H2O2} =		0.09

Table 2. (continued)

Alkene	Reference	Product Yield		
Isoprene	*Gab et al.* [1995]	Y_{H2O2} =	0.007	
	Becker et al. [1990]	Y_{H2O2} =	0.0004	0.001
	Hewitt and Kok [1991][c]	Y_{H2O2} =		0
	Grosjean et al. [1993a]	Y_{MAC} =		0.44
		Y_{MVK} =		0.17
	Aschmann and Atkinson [1994]		RH = 3-7%	
		Y_{MAC} =	0.387	
		Y_{MVK} =	0.159	
	Rickard et al. [1999]		Dry	
		Y_{MAC} =	0.32	
		Y_{MVK} =	0.13	

[a] RH < 0.5% unless otherwise stated
[b] RH > 50% unless otherwise stated
[c] Yield relative to alkene consumption, no OH scavenger

Experiment

A detailed description of the experimental setup is given in our companion paper [*Hasson et al.*, this issue]; hence only a brief outline is given here. The gas phase ozone-alkene reactions were carried out in a 240 L pillow-shaped Teflon reactor. Zero air at the required relative humidity (RH) was generated with a water bubbler. Alkenes were introduced into the reactor at concentrations between 5 and 25 × 10^{13} molecules cm^{-3}. The majority of experiments were carried out in an excess (>5 × 10^{16} molecules cm^{-3}) of cyclohexane, to scavenge >98% of any OH radicals produced in the ozone-alkene reactions. Butyl ether scavenged OH in methylene cyclohexane experiments. The concentrations of hydro carbons and > C_1 carbonyl compounds were determined using a gas chromatograph with flame ionization detection (GC-FID) (Hewlett-Packard 5890). Concentrations were calculated by using each organic compound's effective carbon number.

In a typical experiment, ozone was added until about 75% of the alkene initially present had reacted. A dilute (~2%) ozone in O_2 mixture was generated by passing pure oxygen (ASG, ultra high purity) over a low-pressure mercury pen-ray lamp (Jelight Company). The ozone was introduced either in a single addition or in 5-6 aliquots depending on the lifetime of the alkene with respect to reaction with O_3.

Concentrations of H_2O_2 and organic hydroperoxides were determined by reversed phase high performance liquid chromatography (HPLC) with fluorescence detection [*Gab et al.*, 1985]. Hydroperoxides were scrubbed into a dilute phosphoric acid solution using a 1-m-long stripping coil. Samples were withdrawn from the reactor at a flow rate of 3 L min^{-1} for a total of 2 min. The hydroperoxides were then separated as described in our companion paper [*Hasson et al.*, this issue] by HPLC. At the end of the column, a mixture of *para*-hydroxy phenylacetic acid (POHPAA) and horseradish peroxidase was mixed with the column effluent. Hydro peroxides react stoichiometrically with POHPAA in the presence of the enzyme to produce a dimer that fluoresces strongly in alkaline solution. Following complete conversion of the hydroperoxides, quantification was performed using a fluorescence detector. Hydroperoxides were identified by comparison of their retention times with those of authentic standards, and were quantified using standardized H_2O_2 solutions as described in our companion paper [*Hasson et al.*, this issue]. Errors associated with hydroperoxide and carbonyl yields are estimated to be 25% and 5 %, respectively.

In contrast to most of the experiments described in our companion paper [*Hasson et al.*, this issue], experiments were largely carried out in the presence of an excess of cyclohexane to scavenge any OH generated from the ozone-alkene reactions. In such experiments, interference from OH-alkene reactions is avoided, which is a considerable advantage if the OH yield from the ozonolysis reaction is not well known, or if the yields of carbonyl compounds (which are the major products of OH + alkene reactions) need to be measured accurately. The presence of OH and cyclohexane may affect the concentrations of RO_2 radicals present and thus the yields of hydroperoxides. No difference in the presence and absence of cyclohexane for the hydroperoxides of interest was observed from ethene and *trans*-2-butene ozonolysis.

Results

For all of the alkenes investigated, H_2O_2 and hydroxy methylhydroperoxide were the principal hydroperoxides detected. In addition, hydroperoxymethyl formate (HPMF) was observed in all experiments at low humidity. Additional hydroperoxides were observed in the ozonolysis of 1-butene and isoprene only. Product yields, relative to alkene reacted, were obtained by linear regression analysis. For all of the reported values, plots of product concentrations versus alkene reacted with ozone showed good linearity implying that decomposition or reaction of the products was negligible.

For all of the alkenes investigated (with the exception of camphene, discussed below), the general trends in product yields as a function of water concentration, were the same. The dependences of product yields on RH are illustrated in Figures 3-5 and summarized in Table 2. Yields of hydro peroxides are low under dry conditions (typically below 5 and 1% for H_2O_2 and for HMHP, respectively). As the water concentration is increased, the yields of these compounds rise, approaching a limiting value at the highest humidities investigated. The yield of the carbonyl compound (generated partly from the cycloreversion of the primary ozonide, (R2)) was generally found to be dependent on the relative humidity. For most compounds, the increase in carbonyl yield with RH was, within experimental uncertainties, identical to the increase in the yield of H_2O_2. The specific behavior of each alkene is discussed below.

1-Butene

At 0% RH, the yields of hydroxymethyl hydroperoxide (HMHP), H_2O_2, and propanal from 1-butene ozonolysis are

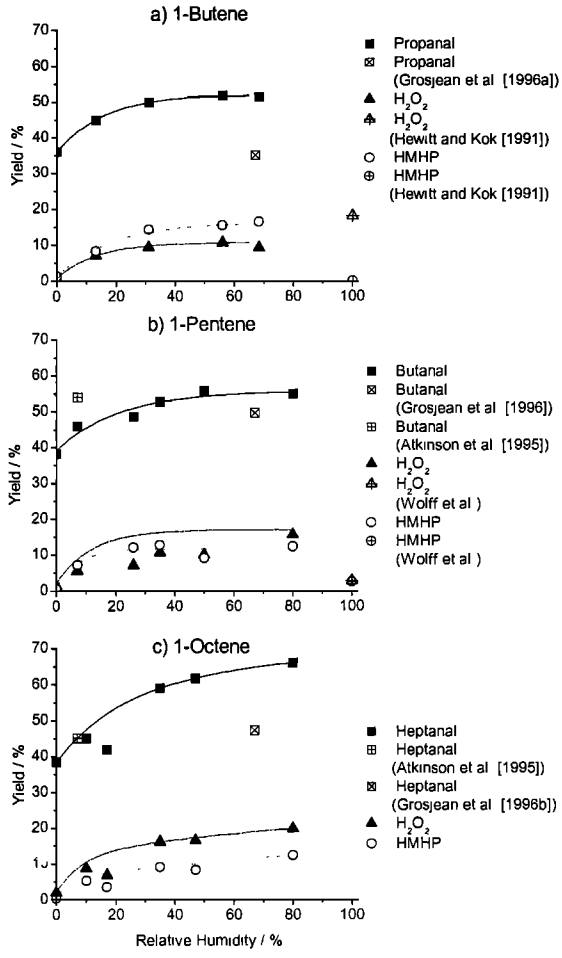


Figure 1. Dependence of product yields on the relative humidity in the ozonolysis of a) 1-Butene, b) 1-Pentene, and c) 1-Octene. Selected literature values are included for comparison.

0.007, 0.013, and 0.36, respectively; as the humidity increases, the yields of all three products rise, reaching their upper limits of 0.15, 0.11, and 0.52 , respectively, at about 40% relative humidity (RH) (see Figure 1a). A trace quantity of methyl hydroperoxide (MHP) and an additional peak with a 1% yield were observed (not shown), independent of RH. The latter peak is believed to be either ethyl hydroperoxide (EHP) or 2-hydroperoxypropanal.

There have been two previous studies of hydroperoxide formation from 1-butene ozonolysis. *Becker et al.* [1993] measured H_2O_2 yields under humid conditions by Fourier transform infrared (FTIR) and diode laser spectroscopy, while *Hewitt and Kok* [1991] measured hydroperoxide yields in the presence of bulk water by HPLC. H_2O_2 was not detected by either study. Hewitt and Kok obtained a total yield of HMHP in gas, aerosol, and wall-adsorbed phases of about 0.18, in good agreement with this work. Their yields of MHP and EHP (approximately 0.03 and 0.16) are, however, substantially higher than those obtained in this work.

There are two literature values for propanal yields from the ozonolysis of 1-butene. The value of 0.35, reported by *Grosjean et al.* [1996a], is inconsistent with the yields reported here since the experiments were performed under humid conditions (~67% RH). Our previously published propanal yield of 0.45 [*Paulson et al.*, 1999] (~10% RH) is indistinguishable from the corresponding experimental results reported here under the same conditions.

1-Pentene

At 0% RH, HMHP, H_2O_2, and butanal yields of 0.006, 0.014, and 0.38 were obtained from 1-pentene ozonolysis (Figure 1b), respectively. The yields of these compounds rise as the humidity increases and approach their maximum values of 0.13, 0.16, and 0.55, respectively, again at about 40% RH. Under dry conditions, HPMF was observed, and no other hydroperoxides were detected. Only one previous investigation of hydroperoxide yields from 1-pentene ozonolysis has been reported. At 100% RH, *Wolff et al.* [1996] reported very low yields of H_2O_2 and HMHP (0.028 and 0.025, respectively) compared with those determined in this study. They also detected an additional five hydroperoxides (including methyl, and ethyl and 1-propyl hydroperoxide) with a combined yield of 0.09. *Atkinson et al.* [1995] and *Grosjean and Grosjean* [1996] have reported butanal yields of 0.54 and 0.50 from 1-pentene ozonolysis in the presence of water vapor (3-7% RH and 67% RH, respectively). While the butanal yields from Atkinson et al., Grosjean and Grosjean, and this study are all in agreement within their mutual uncertainties, our value at low RH is markedly lower than that of Atkinson et al. (0.38 versus 0.54, respectively). In contrast, our value at high RH is higher than that of Grosjean and Grosjean (0.55 versus 0.50, respectively).

1-Octene

In the absence of water vapor, yields of HMHP, H_2O_2, and heptanal of 0.003, 0.021, and 0.38 were obtained in investigations of 1-octene ozonolysis, respectively. As shown in Figure 1c, the yields of these compounds rise to 0.12, 0.2, and 0.66, respectively, at high humidity. To our knowledge, there are no values for hydroperoxide yields from 1-octene ozonolysis in the literature. Atkinson and coworkers (unpublished work, 2001) have detected 1-hydroxyheptyl hydroperoxide from 1-octene ozonolysis in humid air, but the yield was not obtained. The heptanal yield of 0.52 reported by *Atkinson et al.* [1995] at 3-7% RH is in reasonable agreement with the equivalent value reported in this study (0.45 at 7% RH). However, the yield of 0.47 reported by *Grosjean et al.* [1996b] at 67% RH is substantially lower than the high RH yield measured in this work (0.66).

Methylene Cyclohexane

Methylene cyclohexane ozonolysis provided HMHP, H_2O_2, and cyclohexanone yields of 0.005, 0.035, and 0.19, respectively, at 0% RH; as shown in Figure 2a, these values rise to 0.03, 0.12, and 0.33, respectively with increasing RH, with essentially no change above 30% RH. *Hatakeyama et al.* [1993] measured yields of HMHP and H_2O_2 from the ozone-methylene cyclohexane reaction at 0% RH and 10-17% RH. The reported yields for HMHP (0.0044 at 0% RH and 0.03 at 10-17% RH) are in excellent agreement with our results. Their yield of H_2O_2, however, only increased by about 0.01 as opposed to the much larger increase of 0.08 reported here.

β-Pinene

In the absence of water vapor, the yields of HMHP, H_2O_2, and nopinone from β-pinene are 0.001, 0.03, and 0.26, respectively; the yields of these compounds increase to 0.02, 0.25, and 0.53, respectively, at 80% RH. From Figure 2b, it appears that the yields of these compounds only begin to

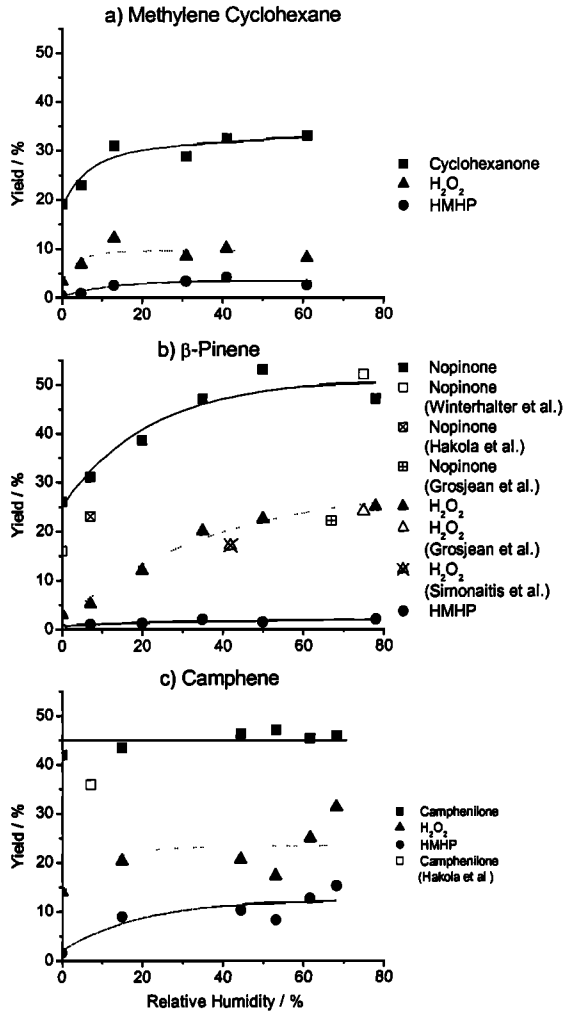


Figure 2. Dependence of product yields on the relative humidity in the ozonolysis of a) Methylene Cyclohexane, b) β-Pinene, and c) Camphene. Selected literature values are included for comparison.

approach their upper limits at the highest humidity investigated. A number of previous studies have investigated hydroperoxide formation in the ozonolysis of β-pinene. In dry air (10 ppm of water), *Gab et al.* [1995] measured a H_2O_2 yield of 0.006. In humid air, *Becker et al.* [1993] measured a H_2O_2 yield of only 0.0015. The remaining measurements are in good agreement with this study. *Hewitt and Kok* [1991] and *Simonaitis et al.* [1991] measured H_2O_2 yields of 0.17 (in the presence of bulk water) and 0.19 (42% RH), respectively. *Winterhalter et al.* [2000] measured the dependence of nopinone and H_2O_2 yields on the water concentration. The behavior that they observed was similar to that reported here, with nopinone and H_2O_2 yields increasing from 0.16 and 0.002 at 0% RH to 0.52 and 0.24 at 83% RH, respectively. Finally, *Grosjean et al.* [1993b], *Hakola et al.* [1994], and *Rickard et al.* [1999] obtained nopinone yields of 0.22 (67% RH), 0.23 (3-7% RH), and 0.23 (0% RH), respectively; the high-humidity measurement [*Grosjean et al.*, 1993b] is less than half of our measured value, while the low-humidity values [*Hakola et al.*, 1994; *Rickard et al.*, 1999] are in good agreement with our work.

Camphene

The results from our camphene experiments were highly scattered. These experiments are difficult to perform since camphene and its oxidation products have relatively low volatilities, thus deposition to the chamber walls is enhanced. Also, the ozone-alkene reaction is extremely slow ($k_1 = 9 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}) [*Atkinson*, 1997]; thus high ozone concentrations are required to limit the lifetime of the alkene to a few hours. The elevated ozone may lead to artifact hydroperoxide formation from aqueous phase O_3 reactions.

Under dry conditions, the yields of H_2O_2, HMHP, and camphenilone were 0.14, 0.02, and 0.42, respectively. At 70% RH, the H_2O_2 and HMHP yields increased to 0.31 and 0.15, respectively (Figure 2c). In contrast to this, the yield of camphenilone was essentially unchanged (0.46). There are no literature values for hydroperoxide yields from these compounds and only a single value for the yield of camphenilone (0.36) at 3-7% RH [*Hakola et al.*, 1993], in reasonable agreement with this work.

Isoprene

A number of hydroperoxides were measured in the ozonolysis of isoprene including H_2O_2, HMHP, methyl hydroperoxide, peracetic acid, and HPMF. The variation of Y_{H2O2} and Y_{HMHP} with relative humidity is shown in Figure 3. The yield of H_2O_2 increases from 0.05 at 0% RH to 0.12 at 60% R.H. Further increases in relative humidity do not affect Y_{H2O2}. Y_{HMHP} rises from 0.01 at 0% RH to 0.16 at 78% RH Similar to ethene, the HMHP yield from isoprene reaches its maximum value at ~20% RH. MHP and PAA represented less than 5% of the total hydroperoxide signal in all experiments.

The yields of methacrolein (MAC) and methyl vinyl ketone (MVK) were found to be dependent on RH as well. In the absence of water vapor, Y_{MAC} and Y_{MVK} were found to be 0.35 and 0.17, respectively; under humid conditions, these yields rose to 0.42 and 0.24 respectively (Figure 3).

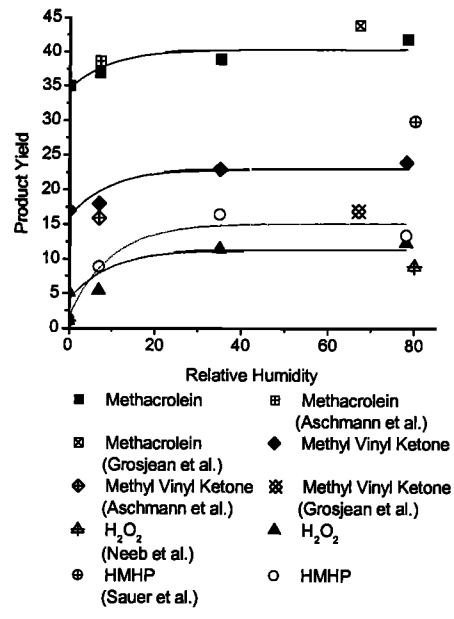


Figure 3. Dependence of product yields on the relative humidity in the ozonolysis of isoprene. Selected literature values are included for comparison.

Several studies have investigated the effects of humidity on the ozone-isoprene reaction, reflecting the atmospheric importance of this compound. Literature values are summarized in Table 2. H_2O_2 yields are in good agreement with those obtained by *Simonaitis et al.* [1991] and *Sauer et al.* [1999]. Carbonyl yields are also in good agreement with results obtained by Sauer et al. However, the HMHP yield obtained here under humid conditions is only about half of the value reported by *Neeb et al.* [1997].

Discussion

The marked dependence of the yields of HMHP, H_2O_2, and carbonyl compounds on the water vapor concentration in the ozonolysis of alkenes can be explained by the reaction of CIs with water (R6). In the absence of water vapor, carbonyl compounds are formed solely in the primary ozonide cycloreversion reaction (R2), and H_2O_2 is formed only by the self-reaction of hydroperoxy radicals (R7);

(R7) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$.

SCIs either undergo unimolecular decomposition or react with other compounds such as formaldehyde, aldehydes/ketones, and formic acid. The reaction of SCIs with water to produce α-hydroxyalkyl hydroperoxides (R6a), carbonyl compounds and H_2O_2 (R6b), and carboxylic acids (R6c) can compete with the other loss processes for the SCIs. Thus as the humidity increases, so does the yields of these products. At a specific humidity, the yields of hydroperoxides, carbonyl compounds, and carboxylic acids are thus determined by the SCI yield from the ozone-alkene reaction, the relative rates of the reactions of the SCIs, and the branching ratios for the SCI-water reactions (R6). In contrast to this work, previous measurements (as summarized by *Atkinson* [1997] and illustrated in Figures 3-5) do not reveal systematically higher carbonyl yields at higher humidities. In general, the results from the Atkinson group are in good agreement with this study, whereas Grosjean et al. carbonyl yields are lower than those reported here. The Grosjean studies used DNPH-coated C18 cartridges to derivatize the carbonyl compounds and then analyzed the products by liquid chromatography with uv-visible detection. This technique is liable to have greater uncertainties associated with it than the more common and direct GC-FID method, which may explain the discrepancies between our high-RH data and those of Grosjean and coworkers.

In the experiments described here, large α-hydroxyalkyl hydroperoxides produced by the reaction of water with SCIs (R6a) would not be detected because of their rapid aqueous decomposition to H_2O_2 and a carbonyl during sampling. The fate of large α-hydroxyalkyl hydroperoxides in the GC-FID inlet and GC column is less clear, but they do not survive to be analyzed as hydroperoxides at the end of the column. They may either be lost to the GC inlet/column, or they may decompose, possibly to the corresponding carbonyl and H_2O_2 heterogeneously and be analyzed as carbonyls:

(R8) $RCH(OH)OOH(aq) \rightarrow RCHO(aq) + H_2O_2(aq)$.

Where comparison is possible, the carbonyl yields measured by GC-FID are in good agreement with literature values measured by FTIR [*Atkinson*, 1997; *Winterhalter et al.*, 2000], where the decomposition of α-hydroxyalkyl hydroperoxides likely does not occur. For camphene, an increase in H_2O_2 yields is observed as the humidity is increased, but this is not matched by an increase in the yield of camphenilone. This suggests that the hydroxyalkyl hydroperoxide is formed and is stable within the chamber on the timescale of the experiments. Since this large hydroxyalkyl hydroperoxide does not decompose to camphenilone in the GC column, it could be argued that the carbonyl compounds measured in other reactions originate solely from gas phase ozone-alkene chemistry and not from hydroxyalkyl hydroperoxide decomposition in the column.

Table 3. Stabilized Criegee Intermediate Yields from Ozone-Alkene Reactions

Alkene	Reference	Y_{SCI}
1-Butene	This Study	0.27
1-Pentene	This Study	0.29
1-Octene	This Study	0.35
	[*Paulson and Seinfeld*, 1992]	0.22
Methylene Cyclohexane	This Study	0.14
	[*Hatakeyama and Akimoto*, 1994]	0.26
β-Pinene	This Study	0.27
	[*Hatakeyama and Akimoto*, 1994]	0.25
Camphene	This Study	0.30
Isoprene	This Study	0.26

Stabilized Criegee Intermediate Yields

The major products of the reaction of SCIs with water are HMHP for CH_2OO, and H_2O_2 plus an aldehyde or ketone for larger CIs. Changes in the yields of these compounds with increasing RH can consequently be used to infer the yields of SCIs from ozone-alkene reactions. Provided that the hydroperoxide yields have reached their maxima at the highest humidities investigated, the yield of stabilized CH_2OO is given by the difference in the yield of HMHP at high and low humidity [*Hasson et al.*, this issue]. The SCI yield for the larger fragment is given by the difference in the yields of H_2O_2 or the corresponding carbonyl under dry and humid conditions. SCI yields inferred this way are given in Table 3.

A comparison between our SCI yields presented here and literature OH yields reveals that there is an anticorrelation between these two quantities from ozone-alkene reactions, as has been noted previously [*Paulson et al.*, 1999; *Rickard et al.*, 1999]. This relationship is illustrated in Figure 4. Here we develop a simple structure-activity relationship to predict OH yields from ozone-alkene reactions based on the ability of the corresponding CIs to rearrange to a vinyl hydroperoxide via reaction (R3) [*Paulson et al.*, 1999; *Rickard et al.*, 1999]. CIs capable of undergoing this rearrangement (i.e. *syn*-carbonyl oxides) are assumed to generate OH with a yield of unity, while *anti*-carbonyl oxides, which cannot rearrange via (R3), are assumed to generate no OH. The yield of OH from CH_2OO is assumed to equal that from the ethene-ozone

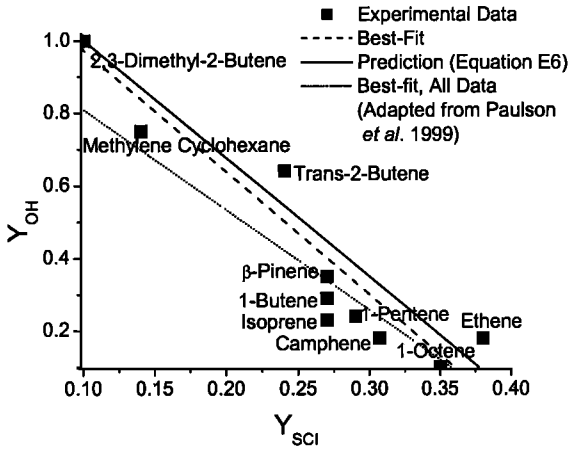


Figure 4. Relationship between yields of OH radicals and stabilized Criegee intermediates in the ozonolysis of alkenes.

reaction. The apparent link between the OH and SCI yields suggests that a similar structure-activity relationship should exist to explain the yields of SCIs based on their structure. Here the assumption is made that all *syn*-Criegee intermediates capable of rearranging to a vinyl hydroperoxide (R3) produce the same fraction of SCI. This value is taken to be 0.1: the SCI yield from 2,3-dimethyl-2-butene ozonolysis, where the yield of this type of CI is unity. Such CIs are denoted CIa. CIs that cannot undergo rearrangement to a vinyl hydroperoxide are denoted CIb and include CH_2OO, *anti*-carbonyl oxides, and *syn*-carbonyl oxides where no hydrogen atoms are available to undergo this rearrangement. The fraction of stabilized CIb is taken to be 0.39: the SCI yield from ethene ozonolysis, where the yield of CIb is unity. The SCI yield is therefore predicted to be:

$$Y_{SCI} = 0.1 \times Y_{CIa} + 0.39 \times Y_{CIb}. \quad (1)$$

For alkenes that produce several different CIs, the yield of each is equated to the yield of the corresponding carbonyl cogenerated in the primary ozonide cycloreversion at 0% RH (R2). For a specific CI, the yield of *syn*- and *anti*-carbonyl oxide is assumed to be equal. Although this may not be precisely correct [*Fenske et al.*, 2000b; *Rathman et al.*, 1999], our intention is to develop a method of predicting SCI yields without the need for detailed experiments and calculations.

To clarify the protocol for predicting SCI yields based on alkene structure, the method is illustrated for 1-butene. This alkene can generate three different carbonyl oxides: CH_2OO, and *syn*- and *anti*-CH_3CH_2CHOO. At 0% RH, the yield of propanal from 1-butene ozonolysis is 0.36, hence the yield of CH_2OO (cogenerated with propanal in (R2)) is also 0.36. The combined yield of *syn*- and *anti*-CH_3CH_2CHOO is therefore 0.64, and assuming that each isomer is produced in equal quantities, the yields of *syn*- and *anti*-CH_3CH_2CHOO are both 0.32. The fraction of CIa is therefore 0.32 (the yield of *syn*-CH_3CH_2CHOO) and the fraction of CIb is 0.68 (the sum of the yields of *anti*-CH_3CH_2CHOO and CH_2OO), and the predicted SCI yield is $0.1 \times 0.32 + 0.39 \times 0.68 = 0.30$. A comparison between predicted and measured SCI yields is shown in Figure 5. Agreement is generally very good, confirming the validity of this approach.

Earlier in this section, the procedure for estimating OH yields from ozone-alkene reactions was outlined. This can be represented mathematically by

$$Y_{OH} = Y_{CIa} + 0.18 \times Y_{CH2OO}. \quad (2)$$

If the assumption is made that the yields of *anti*-carbonyl oxide and CH_2OO are equal, then the OH yield from CIb will be 0.09 (since *anti*-carbonyl oxide is assumed to generate no OH), and equation (2) may be simplified:

$$Y_{OH} = Y_{CIa} + 0.09 \times (1 - Y_{CIa}). \quad (3)$$

Clearly, this assumption is not valid for all of the alkenes investigated. For internal alkenes, no CH_2OO is produced, and the OH yield from CIb is 0, while for ethene, no *anti*-carbonyl oxide is produced, and the OH yield from CIb is 0.18. It is worth noting, however, that *anti*-carbonyl oxide may well generate some OH, and that varying the OH yield from CIb between 0 and 0.18 has a noticeable but not dramatic effect on the structure-activity relationship. The corresponding expression for the yield of SCI is obtained by substituting ($1-Y_{CIa}$) for Y_{CIb} in equation (1):

$$Y_{SCI} = 0.1 \times Y_{CIa} + 0.39 \times (1 - Y_{CIa}). \quad (4)$$

Eliminating Y_{CIa} from equations (3) and (4) leads to an expression directly relating the yields of OH and SCI from ozone-acyclic alkene reactions:

$$Y_{OH} = 1.325 - 3.25 \times Y_{SCI}. \quad (5)$$

This expression is plotted along with experimental values of these yields in Figure 4. The agreement between equation (5) and the least squares fit to the experimental data is very good. Also included for comparison is the best-fit line for all literature values of OH and SCI yields adapted from [*Paulson et al.*, 1999] (with cyclic alkenes removed and ethene added). The trendline is similar to that determined in this study.

Atmospheric Fate of Stabilized Criegee Intermediates

In the absence of significant SO_2 levels, the primary sinks for SCI are unimolecular decomposition and reaction with water (R6) (and possibly reactions with NO_x); thus the results presented here can be used to predict yields of hydroperoxides in the troposphere under reasonably clean conditions. It can be shown that the hydroperoxide yield is related to the SCI yield and water concentration by the expression

$$Y_{hydroperoxide} = Y_{SCI}\left(\frac{k_{uni}}{k_6[H_2O]} + 1\right)^{-1}, \quad (6a)$$

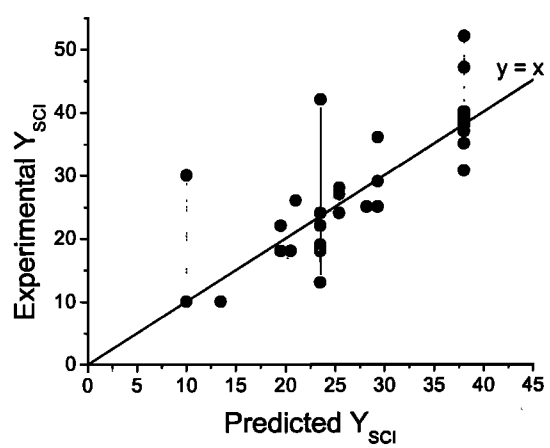


Figure 5. Comparison of experimental and predicted product yields in the ozonolysis of terminal alkenes. Vertical dashed lines join different literature values for the same quantity.

where $Y_{hydroperoxide}$ is the yield of HMHP or H_2O_2, Y_{SCI} is the yield of the corresponding SCI, $[H_2O]$ is the mixing ratio of water in ppm, and k_{uni} and k_6 are the rate coefficients for unimolecular decomposition of the SCI and bimolecular reaction with water, respectively. Thus by plotting $Y_{SCI}/Y_{hydroperoxide}$ against $1/[H_2O]$ for all of the experiments, a linear plot is obtained from which an average value of k_{uni}/k_6 for all of the SCIs generated in these experiments may be determined. From this analysis, we recommend the following expression (6b) to describe the dependence of hydroperoxide yields on relative humidity, in atmospheric models, but note that this represents an upper limit, since the reactions of SCIs with other trace species (NO_x, SO_2, etc.) are not considered:

$$Y_{hydroperoxide} = Y_{SCI}\left(\frac{2870}{[H_2O]}+1\right)^{-1}. \qquad (6b)$$

The estimate for k_{uni}/k_6 can be compared to previous measurements of these rate coefficients. In a previous publication from this laboratory [*Fenske et al.*, 2000a], k_{uni} was determined to be 80 s^{-1} for CH_3CHOO. This leads to an estimate for k_6 from this work of 1.1 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}, which lies at the upper end of the range of estimates for this reaction (as summarized by *Fenske et al.* [2000a]). It is important to note, however, that both of these rate coefficients are likely to vary substantially depending on the structure of the CI and that the "average" value for the ratio determined here is intended primarily to enable the incorporation of this chemistry into atmospheric models.

Product Yields in the Ozonolysis of Linear 1-Alkenes

In a recent publication from this laboratory [*Paulson et al.*, 1999], we noted that the yield of OH from the ozonolysis of 1-alkenes is inversely related to the carbon chain length. The hydroperoxide yields measured here for 1-butene, 1-pentene, and 1-octene appear to offer a possible explanation for this trend. The yields of HMHP (at high RH) and aldehyde (at 0% RH) are approximately the same for the three compounds, indicating that the total yields of CH_2OO and larger CI are invariant along the 1-alkene series. The yield of H_2O_2 at high RH, however, increases along the series (from 0.11 to 0.2). In addition, the difference between the dry and humid aldehyde yields increases from 0.16 to 0.28. These observations are consistent with an increase in the proportion of *anti*-carbonyl oxide relative to *syn*-carbonyl oxide, which would result in a decrease in OH yields, as the carbon chain length increases.

To investigate the reasons for this switch from *syn*- to *anti*-carbonyl oxide as the carbon chain length increases, simple RRK calculations [*Holbrook et al.*, 1996] were performed.

Table 4. B3LYP/6-31G(d,p) Reaction Energies for Primary Ozonide Formation and Cycloreversion Activation Barriers (kilocalories per mole) Used in RRK Calculations

Alkene	Reaction Energy	Activation Energy			
		R2a	R2b	R2c	R2d
1-Butene	-56.6	17.2	18.0	18.8	19.3
1-Pentene	-56.6	17.0	17.9	18.7	19.2
1-Octene	-56.6	16.9	17.8	18.6	19.1

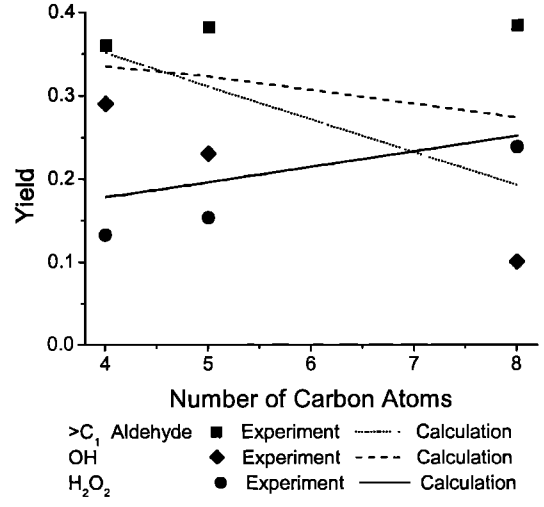


Figure 6. Comparison of experimental product yields and RRK calculations in the ozonolysis of straight-chain terminal alkenes.

Yields of the different CIs were calculated from the cycloreversion pathways of the primary ozonides (R2) using equation (7):

$$Y_i = \frac{\nu^*\left(\frac{E-E_{Ai}}{E}\right)^{s-1}}{\sum_i \nu^*\left(\frac{E-E_{Ai}}{E}\right)^{s-1}}, \qquad (7)$$

where Y_i is the branching ratio for pathway i at energy E, ν^* is the frequency of the vibrational mode at the transition state corresponding to motion along the reaction coordinate, E_{Ai} is the activation energy for the unimolecular reaction channel i, and s - 1 is the number of available vibrational modes at the transition state. The initial energies of the primary ozonides (E, equal to –56.6 kcal/mol for all three alkenes) and activation energies for the cycloreversion reactions (E_{Ai}) were obtained from density functional theory calculations and are summarized in Table 4. The number of available vibrational modes at the transition state (s) was taken to be half of the number of normal modes in the primary ozonide. Equations (2) and (3) were then used to determine the yields of aldehyde, OH, and H_2O_2 expected from these calculated CI yields. Experimental and calculated yields are compared in Figure 6. As can be seen in Figure 6, the calculations reproduce some of the observed trends in product yields.

As can be seen from Table 4, the cycloreversion pathways leading to CH_2OO and the large aldehyde (R2c) are the least favorable. The activation energy for the formation of *syn*-carbonyl oxide and formaldehyde is smaller (R2b), while *anti*-carbonyl oxide and formaldehyde production (R2a) is the most facile. The initial energy of the primary ozonides and the activation energies of the four cycloreversion pathways are essentially identical along the 1-alkene series. However, as the size of the primary ozonide increases, the lowest-energy pathway becomes increasingly favored entropically (due to the higher density of states for larger ozonides), and the yield of *anti*-carbonyl oxide increases at the expense of *syn*-carbonyl oxide and CH_2OO. These calculations go part way toward explaining the observed trends in the product yields. A

more sophisticated treatment may, however, more fully explain the decrease in OH yields along the 1-alkene series.

Conclusions

In this and our companion paper, formation of H_2O_2 and organic hydroperoxides has been extensively studied for a range of different alkenes at different humidities. The results of these experiments have been used to develop a structure-activity relationship to estimate SCI yields and consequently H_2O_2 and organic hydroperoxide yields from the ozonolysis of exocyclic alkenes. We have also shown that this model is consistent with the existing structure-activity relationship proposed to explain OH yields from ozone-alkene reactions.

Based on the experimental evidence presented here, it appears that the broad features of the chemistry of CIs are determined by the availability of the isomerization channel that leads to production of OH. Yields of OH and SCIs, and possibly rate coefficients for the unimolecular decomposition of SCIs, are controlled by the availability of this reaction pathway. As a consequence of this, the complex chemistry of OH radical and hydroperoxide formation from ozone-alkene reactions can be parameterized for incorporation into atmospheric models.

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A. S. Hasson, Department of Chemistry, California State University, Fresno, 2555 East San Ramon M/S SB70, Fresno, CA93740-8034, USA. (ahasson@csufresno.edu)

A. W. Ho, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA. (aho@fas.harvard.edu)

K. T. Kuwata, Department of Chemistry, 1600 Grand Avenue, Macalester College, St. Paul, MN 55105-1899, USA. (kuwata@macalester.edu)

S. E. Paulson, Atmospheric Sciences Department, University of California at Los Angeles, Math Sciences Building, 405 Hilgard Avenue, Los Angeles, CA 90095-1565, USA. (paulson@atmos.ucla.edu)

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