Photochemical Sources of Organic Acids. 2. Formation of C_5-C_9 Carboxylic Acids from Alkene Ozonolysis under Dry and Humid Conditions

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The dependence of organic acid generation by alkene ozonolysis on relative humidity, thermalized Criegee intermediate scavengers, and alkene structure is investigated. Carboxylic acids generated from the ozonolysis of 1-hexene, 1-octene, 1-decene, *trans*-3-octene, and 1-methylcyclohexene were analyzed as trimethylsilyl (TMS) derivatives. Experiments were performed under dry (relative humidity (RH) < 1%) and humid (RH = 65%) conditions with cyclohexane or *n*-butyl ether as an OH scavenger. Pentanoic acid is produced from 1-hexene and *trans*-3-octene with yields 8.5 ± 2.6 and 5.0 ± 1.5% under dry conditions and 5.1 ± 1.5 and 2.8 ± 0.8% under humid conditions, respectively. Heptanoic acid yields from 1-octene are 8.3 ± 2.5 and 4.4 ± 1.3% under dry and humid conditions, respectively. Ozonolysis of 1-methylcyclohexene produced six C_5-C_7 multifunctional carboxylic acids, with a total yield of 7%. Several other acids and aldehydes were also monitored and quantified. An additional set of experiments with added stabilized Criegee intermediate (SCI) scavengers was performed for 1-octene ozonolysis under dry conditions. The results indicate that SCIs and their reaction with water are minor contributors to acid formation in the atmosphere and suggest that many of the acids are formed directly.

1. Introduction

Organic acids are ubiquitous, not only in the gas phase and in clouds and in rain but also in aerosols. Formic and acetic acids are the most abundant, but larger mono- and diacids up to C_{11} have been detected in samples from around the globe.[1−3] Field and experimental measurements of carboxylic acids produced by O_3 reactions with biogenic terpenes point to their key role in secondary aerosol formation.[4] Several possible sources have been suggested for organic acids in the atmosphere. The largest of these sources include direct anthropogenic emissions,[5,6] biogenic emissions[7,8] biomass burning,[9] and homogeneous oxidation of hydrocarbons.[10,11] The contribution of each source remains very uncertain and likely location-dependent.[12−14]

Ozone reactions with alkenes, the focus of this work, together with HO_2 reactions with acylperoxy radicals are generally assigned as the dominant photochemical acid production pathways.[12,15−19] The ozone−alkene source has been thought to arise from the reaction of a so-called stabilized Criegee intermediate (SCI) reacting with water.[20−22] Recent quantum chemical calculations by Anglada et al.[23] further support the notion that acids should be a major product of stabilized Criegee intermediates reacting with water. However, recent studies of the ozonolysis of several alkenes suggest that acid formation from this pathway may instead be quite limited, with the dominant products identified as hydroperoxides instead (see refs 24−26, and references therein).

Organic acid production from O_3 reactions with alkenes was observed as early as 1977 by Herron and Huie.[10] Since then, a number of studies have reported acid formation. Several of these have focused on formation of formic and acetic acid from ethene, propene, and *trans*-2-butene[10,27−31] and are in reasonable agreement with one another.

Prior to this one, no studies of acid formation by larger acyclic alkenes have been performed; acid formation from larger alkenes has focused almost entirely on monoterpenes.[4,32−36] A handful of studies have also investigated smaller cyclic compounds such as cyclohexene and methylcyclohexene.[4,37,38] All studies of cyclic alkenes find formation of both mono- and diacids, the monoacids having a C_{N-0} or C_{N-1} carbon backbone and the diacids a C_{N-1} or C_{N-2} carbon backbone, together with appropriate carbonyl and/or hydroxy groups. Reported yields vary by more than an order of magnitude, but are uniformly small; for example, yields of pinic and pinonic acids from α-pinene ozonolysis fall in the ranges 0.1−4 and 0.2−8%, respectively.[4,32−36] A few studies have investigated the dependence of acid formation on the presence of an OH scavenger or on relative humidity (RH). Generally acids are observed to decrease with added scavenger and RH, although studies are not in agreement on the quantitative aspects of these issues.[4,32,35,36,]

To investigate the fundamental aspects of acid formation and its dependence on RH, organic acids from ozonolysis of 1-hexene, *trans*-3-octene, 1-octene, 1-decene, and 1-methylcyclohexene under dry and humid conditions were quantified. To further elucidate a probable pathway to acid formation, experiments with added stabilized Criegee intermediate scavengers were performed for 1-octene ozonolysis under dry conditions. Sampling of carboxylic acids was carried out with midget bubblers containing a solution of dodecane (internal standard) in ethyl acetate. Ozonolysis experiments were performed under dry (RH < 1%) and humid (RH = 65%) conditions, and cyclohexane or *n*-butyl ether were used as OH scavengers. The

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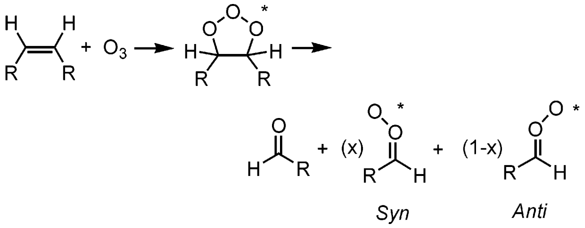
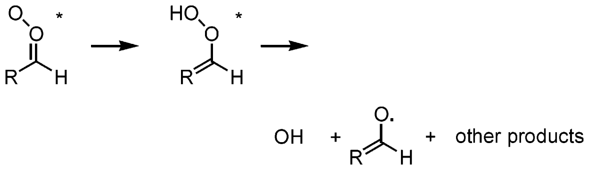
quantitative analyses of collected samples were performed using a gas chromatograph/flame ionization detector/mass spectrometer (GC/FID/MS). Carboxylic acid and hydroxy groups were analyzed after in-inlet derivatization, based on the approach developed by Docherty and Ziemann.[39]

(1.1) Formation Pathways of Carboxylic Acids. The mechanism of ozonolysis and potential pathways for production of organic acids is discussed in detail in the companion paper in this issue,[40] thus it is described only briefly here. The reaction of ozone with alkenes is initiated with its 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 (CI). The nascent Criegee intermediate is believed to adopt the carbonyl oxide structure.[41]



(R1)

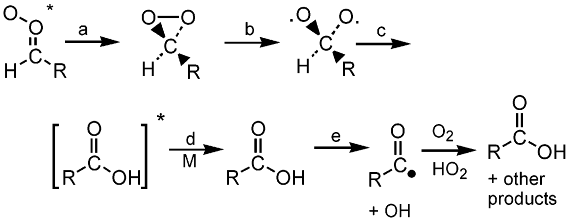
This reaction (R1) is highly exothermic; thus, a number of unimolecular isomerization and decomposition channels are thermodynamically accessible to CIs (R2 and R3). The most important decomposition pathway for *syn*-carbonyl oxides produces OH radicals:



(R2)

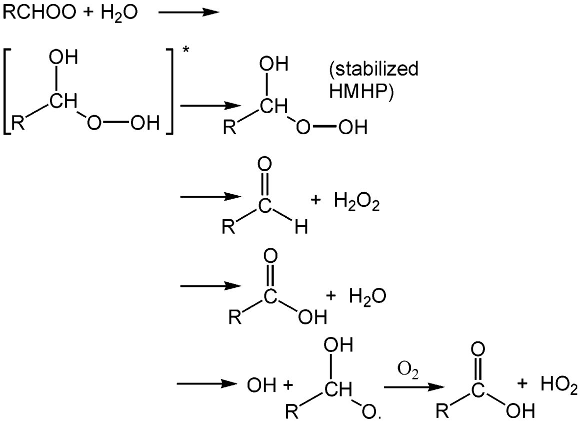
OH radical yields from the alkenes investigated here are as follows: 1-hexene, 18%; 1-octene, 10%; 1-methylcyclohexene, 90%.[42,43] OH from *trans*-3-octene has not been measured, but it can be estimated by analogy with *trans*-3-hexene, the most similar compound for which an OH yield has been measured, at around 50%.[44]

The lowest barrier available to *anti*-carbonyl oxides is isomerization to dioxirane, at about 20 kcal/mol.[45] A vibrationally excited carbonyl oxide may rearrange via the dioxirane to the bis-oxy form (R3a−b), and from here, the highly exothermic rearrangement to the acid (R3c−d) is nearly barrierless.[45] Activation energies for decomposition of the hot acids are also small, from 2 to 15 kcal/mol; thus limited stabilization may result in small acid yields. An additional potential pathway to small yields of acids is pathway R3e, whereby the hot acid formed in step R3c decomposes to OH and an acyl radical, and the resulting acylperoxy radical reacts with HO_2 to generate an acid. Several other decomposition pathways compete with R3e, however,[45−47] such that generation of the acyl radical should be small. Further, reaction of acyl radicals with HO_2 generates acids with a yield of only 20−50%;[48] thus, this pathway should be responsible for very small acid yields (<5% and probably less than 1%).



(R3)

A fraction of the nascent CI, likely most of it formed initially as an *anti*-carbonyl oxide,[26] survives long enough to undergo bimolecular reactions. SCIs have lifetimes with respect to decomposition on the order of milliseconds.[49] Stabilized Criegee intermediates (R4) react with a variety of different compounds, often referred to as Criegee scavengers, including sulfur dioxide,[50,51] hexafluoroacetone,[52] aldehydes, alcohols, carboxylic acids, and water.[38,50] SCI yields have been measured for 1-octene and 1-methylcyclohexene at 36 [26] and 10.4 ± 6.5%,[50] respectively. SCI yields of 25 and 33% can be estimated for *trans*-3-octene and 1-hexene, respectively, based on similar compounds and trends established by earlier work from this laboratory.[26,43] For 1-octene, the C_7 SCI accounts for about two-thirds of the total SCI yield.[26,53] Four channels are thermodynamically accessible for the reaction of SCI's with water, all presumably proceeding through the hydroxyhydroperoxide intermediate:



(R4a)

(R4b)

(R4c)

(R4d)

Recently, Anglada and co-workers[23,54] carried out theoretical investigations of the potential energy surfaces for water reacting with CH_2OO and CH_3CHOO. In both cases, they found that water-catalyzed decomposition of the α-hydroxyhydroperoxide to H_2O_2 and aldehyde (R4b) has a lower activation energy than the corresponding decomposition to the acid and water (R4c). However, they conclude that the most facile decomposition pathway for the hydroxyhydroperoxide is RCH(OH)O−OH bond cleavage to produce OH and the $HOCHRO^\bullet$ radical (R4d). $HOCH_2O^\bullet$ and $CH_3CH(O^\bullet)OH$ should rapidly react with O_2 to produce formic or acetic acid and HO_2, respectively (R4d).

Two studies have found no dependence of OH formation from alkene ozonolysis on RH, indicating that R4d is at most a minor channel.[55,56] Instead of decomposing to OH and a radical that is converted to an acid, the hydroxyhydroperoxides appear instead to be stabilized (R4a). Given their large size, the hydroxyhydroperoxides from terpene ozonolysis studied by Aschmann et al.[55] might be expected to undergo stabilization (R4a); however, this process also seems to be dominant for ethene and *trans*-2-butene.[25] On a related topic, quantum chemical examination of the reaction of the C_1 SCI with a water dimer (or the (hydroxymethyl)hydroperoxide−water reaction) led to the conclusion that the main product should be aldehyde + H_2O_2 (R4b), rather than acids (R4c or R4d).[57]

In addition to carboxylic acids produced by the direct pathway (R3) and via reactions of SCI with water (R4c,d), a few other processes expected to generate minor quantities of acids (<0.5%) are discussed in the companion paper in this issue.[40]

2. Experimental Section

(2.1) Chemicals. BSTFA (*N*,*O*-bis(trimethylsilyl)triflouroacetamide) with TMCS (trimethylchlorosilane) (Supelco), anhydrous ethyl acetate and methanol (EM Science), *n*-octylsilane ($C_8H_{17}SiH_3$) (United Technologies), and alkenes, aldehydes, and hexafluoroacetic acid (Aldrich) had 98% or better purity and were used as received.

(2.2) Chamber Experiments. Experiments were carried out at 296 ± 2 K in collapsible Teflon chambers with volumes of 240 or 1300 L in the dark and at atmospheric pressure. The 1300 L chamber was equipped with a Teflon fan. Alkenes and scavengers were evaporated (liquids) or injected (gases) into the matrix air as the chamber was filled and mixed. Experiments performed at RH $< 1\%$ used ultrapure, zero grade cylinder air; for humid air experiments purified air (Thermo-Environmental Model 111) was passed through a fritted-glass water bubbler containing deionized water. Humidity in the reaction chamber was measured with a digital hygrometer (Fisher). The initial hydrocarbon concentrations were determined using a gas chromatograph/flame ionization detector (GC/FID, Hewlett-Packard 5890), equipped with a capillary column (J&W Scientific) DB-1 (0.32 mm i.d., 3 μm film, 30 m) temperature programmed to −50 °C for 0.2 min and then ramped by 14 °C/min to 200 °C and calibrated daily with a cyclohexane standard.[40] After the initial concentrations were established, a series of O_3 aliquots where added. O_3 aliquots were generated by flowing O_2 at 0.2 L/min through a mercury lamp generator (JeLight) and into the chamber, in quantities resulting in 0.5−1 ppm in the chamber. After each addition the chamber contents were mixed manually and allowed to react for 20−30 min and then sampled with the GC/FID, with midget bubblers, and with a solid-phase microextraction device.[40] Experiments lasted 3 h and had average O_3 concentrations of 0.5 ppm or less. The initial concentrations of alkenes ranged from 10 to 18 ppm. Sufficient cyclohexane or *n*-butyl ether was added to scavenge 98% of OH radicals. The FID response[58] normalized to the cyclohexane calibration was used to calculate concentrations of hydrocarbons and carbonyl compounds.

(2.3) Acid Analysis. The technique for in-inlet-based derivatization of carboxylic acids with BSTFA is based on that developed by Docherty and Ziemann.[39] A model 3800 GC/FID coupled with an ion-trap mass spectrometer Saturn 2000 (Varian) was used to identify, and in some cases quantify, carboxylic acid trimethylsilyl derivatives. A Varian-Chrompack CP-Sil5 CB/MS (0.32 mm i.d., 1 μm film, 30 m) column was used to separate compounds. The end of the column was mounted into a TEE connector (Valco), which splits the sample to the MS and FID. The FID was used to monitor sampling efficiency and quantify carboxylic acids, and the MS was used to identify individual acids, unless stated otherwise.

Chromatographic parameters were as follows. The split/splitless injection port with a deactivated glass liner (open, 3.4 mm i.d.) was set at 220 °C. Liquid samples (1 μL of a sample + 1 μL BSTFA, Supelco) were introduced in splitless mode. After 1 min, a split 100:1 was set for 5 min and then reduced to 5:1 for the remainder of the run. The GC oven was temperature programmed starting at 50 °C for 1 min and then ramped at 10 °C/min to a final temperature of 280 °C. The MS acquisition mode contained two segments; a delay segment with adjustable time (usually 0−8.4 min) during which the MS was shut off to protect the filament and multiplier from excess solvent and BSTFA, followed by a segment during which compounds were analyzed. A daily performance of the FID was checked with 1 μL of dodecane (8.5 ng/μL) in ethyl acetate co-injected with 1 μL of BSTFA.

TABLE 1: Derivatization, Trapping, and Sampling Efficiencies for Carboxylic Acids

acid	deriv[a] (%)	trapping (%)	sampling (%)
pentanoic	95.5 ± 6	98 ± 6	100 ± 17
hexanoic	96 ± 6	95	92 ± 11
	98 ± 6*		
heptanoic	89 ± 5	103 ± 11	107 ± 5
octanoic	87 ± 3	95 ± 9	96 ± 8
	92 ± 6*		
malonic	101 ± 7		
	84 ± 4*		
succinic	89 ± 3*		
adipic	90 ± 4*		
6-oxoheptanoic	99 ± 4		
	95 ± 2*		

[a] All derivatization reactions took place in the inlet, with the exception of those marked with an asterisk. These reactions were performed prior to sample injection.

Samples of equilibrated reaction or calibration mixtures were acquired from the reaction chamber by drawing the sample at 1L/min for 15 min through two midget bubblers in series. Each bubbler contained 15 mL of ethyl acetate, spiked with 8.5 ng/μL dodecane. On average, about 10% of the acids carried over to the second impinger; all values reported here are the sums of the two impingers. Dodecane was chosen as the internal reference compound because it did not co-elute with any compounds of interest. The bubbler solvent volume was determined gravimetrically before and after sampling.

The efficiency of the derivatization and the yields of carboxylic acid trimethylsilyl derivatives were calculated using effective carbon number,[58] which is accurate to ∼±10%. That the Si does not contribute to the ECN was verified by injecting *n*-octylsilane solution (0.05 mM) in hexane. TMS groups have been found to have a contribution of 3.0 ECN to the FID signal.[58]

(2.4) Trapping, Sampling, and Derivatization Efficiencies for Acids. There are three primary points at which acids may be lost in the derivatization analysis: They may be deposited in the Teflon chamber, not captured or otherwise lost from the ethyl acetate in the bubblers, or incompletely derivatized in the inlet of the GC. We investigated each process separately, and the resulting trapping, derivatization, and sampling efficiencies are presented in Table 1 for several mono- and diacids and a carbonyl acid, 6-oxoheptanoic acid. For each step, we used both dry and humidified air. No significant difference was observed;[59] thus, the data for the two RHs are combined in Table 1.

Derivatization efficiencies were measured by co-injecting 1 μL of 5−100 μM acid stock solutions with 1 μL BSTFA, as described above. In-inlet derivatization efficiencies calculated this way range from 85 to 98%. In-inlet derivatization efficiencies were also checked by comparing with solutions prepared using an external derivatization.[35] Aliquots of 100 μL each of standard acid solutions with dodecane (internal standard) were introduced into a 2 mL vial with a septum cap, and 50 μL of BSTFA was added. The mixture was placed in a heating block at 60 °C for 40−80 min. Vials were allowed to cool to room temperature, and 1 μL of the resulting sample was injected into the GC. Results for hexanoic, octanoic, and 6-oxoheptanoic acids signals are in very good agreement with those obtained with in-inlet derivatization (Table 1). Calibration curves for concentration ranges of 100 ppb to 2.5 ppm were linear with correlation coefficients of better than 0.98 for all compounds.[59] Derivatization efficiencies for hydroxycarboxylic acids were 85% and

TABLE 2: Initial Concentrations of Alkenes, OH Scavengers, and Formation Yields of Carboxylic Acids and Carbonyl Products From the Ozone−Alkene Reaction under Dry and Humid Conditions

alkene/concn range (ppm)	OH scavenger[a] concn range (ppm)	products	product yields (%)		lit. value(s) (%)
			RH < 1%	RH = 65%	
1-hexene		pentanoic acid	8.5 ± 2.6[c]	5.1 ± 1.5[c]	−
13.7−17.9	2890−5180	pentanal	41 ± 6[c]	57 ± 9[c]	51.8 ± 9.5;[66] 53.6 ± 2.3 [65] (RH = 3−7%)
16.0−17.8	734−2700[b]	butanal	4.4 ± 0.7	4.4 ± 0.7	−
1-octene		heptanoic acid	8.3 ± 2.5	4.4 ± 1.3	obsd, no yields reported[60]
		hexanoic acid	1.8 ± 0.5	1.8 ± 0.5	−
10.7−13.0	2690−3710	heptanal	41 ± 6	53 ± 8	52.7 ± 7;[66] 47.3 ± 2.3 [64] (RH = 3-7%); 38 ± 3 (RH < 1%) and 66 ± 6 (RH = 80%)[26]
		hexanal	4.2 ± 1.5	4.2 ± 1.5	−
1-decene		nonanoic acid	5.3 ± 1.6	3.7 ± 1.1	−
		nonanal	31 ± 5[d]	41 ± 12[d]	49.2 ± 12 (RH = 3−7%)[64]
11.8−14.8	2890−4260	octanoic acid	obsd	obsd	
trans-3-octene		pentanoic acid	5.0 ± 1.5	2.8 ± 0.8	−
		propanal	50 ± 8	62 ± 20	−
11.0−14.9	2620−5180	pentanal	48 ± 7	61 ± 9	−
1-methylcyclohexene		6-oxoheptanoic acid	0.7	0.7	0.7;[e,4] pinonic from α-pinene: 0.4,[36], 0.2,[32] 1.2,[4] 0.2−0.3,[33] 2.2−8;[35] 6-oxohexanoic from cyclohexene: 5.9 [13]
12.9−18.3	1270−2440	hexanedioic acid	1.6	1.8	1.9;[e,4] pinic from α-pinene: 0.6,[36] 1.4,[32] 3.2,[4] 0.1−3,[33] 3−6;[35] pentanedioic from cyclohexene: 5.9 [37]
1.43	43[b]	pentanedioic acid	1.4	1.4	observed;[4] norpinic from α-pinene: 0.04,[32] 0.1;[35] butanedioic from cyclohexene: 0.63 [37]
		5-oxohexanoic acid	1.9	1.7	observed;[4] norpionic from α-pinene: small,[36] 4−13;[35] 5-oxopentanoic from cyclohexene: 4.5 [37]
		6-hydroxyhexanoic acid[f]	0.7	0.7	analogue from cyclohexene: 1 [37]
		5-hydroxypentanoic acid[f]	0.6	0.6	analogue from cyclohexene: 1 [37]
		formic acid	12 ± 2[40]	−	1.9 in aerosol;[4] from cyclohexene: 12 [69]
		acetic acid	6.5 ± 3[40]	−	0.6 in aerosol [4]

[a] Cyclohexane OH scavenger unless stated otherwise. [b] *n*-Butyl ether OH scavenger. [c] Data from experiments with cyclohexane and *n*-butyl ether. [d] Analyzed from impingers. [e] In particles only. [f] Tentative identification.

100% for 10-hydroxydecanoic and 2-hydroxyhexanoic acids, respectively, linear in the range we tested of 0.1−0.5 ppm.

Trapping efficiencies of several acids were established by placing 0.2 μL of the neat acids in a glass tube equipped with two gas connections and a septum cap and heated to 60 °C (Table 1). Dry or humidified air was drawn first through the tube and then through two impingers at the standard sampling rate of 1 L/min for 15 min. Liquid samples from the impingers were analyzed using the in-inlet derivatization procedure described above. On average 10% of the acid carried over into a second impinger. All data presented in this work are the sum of both impingers. Trapping efficiencies are very close to 100%.

Sampling efficiencies were established by evaporating neat acid into the chamber and collecting samples through the impingers after waiting from 25 min to several hours. The data shown in Table 1 are averages of all points and indicate very good recoveries, from 85 to 107%. There were no significant differences in the calculated acid concentrations over periods of a few hours in the Teflon chamber. Some wall losses almost certainly occur (likely of order 10% over a few hours), but since the scatter in the measurements is of the same order, the wall losses are not large enough to be measurable. Further, the scatter in the sampling efficiencies is of the same order as that in the derivatization efficiencies, indicating that derivatization is the primary source of scatter in the data. The problem may not be the derivatization reaction itself but rather the scatter induced by integrating the resulting peaks on the relatively noisy background created by contaminants in the BSTFA.

3. Results and Discussion

Initial alkene concentrations were 10−16 ppm, with sufficient added scavenger to consume 98% of OH radicals (Table 2). Acid yields carry overall uncertainties of ±30% and carbonyls ±15%.

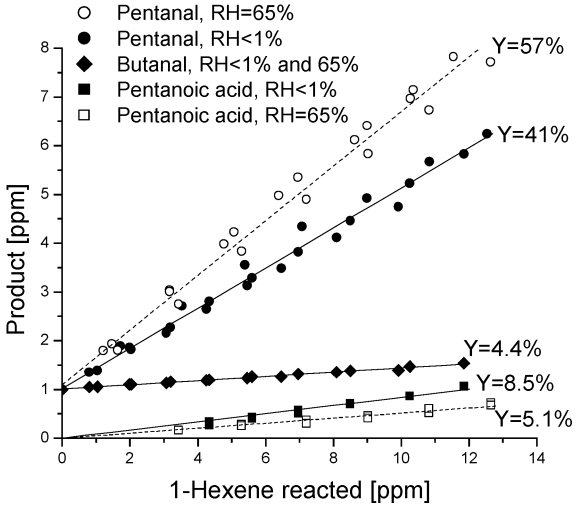


Figure 1. Formation yields of products from 1-hexene ozonolysis under dry (filled symbols) and humid (open symbols) conditions.

(3.1) Terminal Alkenes: 1-Hexene, 1-Octene, and 1-Decene. The C_{N-1} CIs from 1-hexene, 1-octene, and 1-decene result in significant acid formation under dry conditions (Table 2); yields of pentanoic, heptanoic, and nonanoic acids were 8.5 ± 2.6, 8.3 ± 2, and 5.3 ± 1.6%, respectively. Data for 1-hexene are shown in Figure 1 and for 1-octene in Figure 4. Under humid conditions these dropped to 5.1 ± 1.5, 4.4 ± 1.5, and 3.7 ± 1.1%, a decrease of 30−47%. No quantitative acid yields for any of these alkenes have been reported in the literature; however, a product with molecular weight 130 g/mol, which may correspond to heptanoic acid, was observed by Baker et al.[60] in humid air ozonolysis of 1-octene. Also, Paulson and Seinfeld[61,62] suggested that one of the products from 1-octene ozonolysis may have been heptanoic acid, with a yield of ~10%. Losses to walls, sampling lines, or particles for nonanoic acid are not expected to be large on the basis of measured behavior of somewhat smaller homologues heptanal and heptanoic acid. However, losses cannot be ruled out as we did not specifically investigate this possibility.

Formation of the C_{N-2} acid from 1-octene, hexanoic acid (Figure 6), was also observed; yields were 1.8 ± 0.5% for both dry and humid conditions. The analogous acid from 1-hexene was not observable in this study because acid derivatives smaller than C_5 elute under the ethyl acetate and BSTFA peaks. Octanoic acid from 1-decene, although observable in some experiments, could not be quantified because its peak co-elutes with a BSTFA decomposition product. The cycloalkenes have long been observed to generate small quantities of acids with fewer carbon atoms than the parent compound, but this is the first report of the formation of these acids from acyclic compounds.

The work of Winterhalter et al.[24] and Hasson et al.[25,26] indicates that aldehyde yields are quite humidity-dependent. The most likely explanation for this is heterogeneous or homogeneous decomposition of hydroxyhydroperoxides formed in the reaction of water with SCIs (R4). Even if the decomposition is heterogeneous, as suggested by Aschmann et al. [55] and Ziemann and co-workers[38,63] all GC measurements of aldehydes, and likely DNPH derivatization of aldehydes as well,[64,65] are confounded by this source.

Primary aldehyde yields for the terminal alkenes 1-hexene, 1-octene, and 1-decene are 41 ± 6, 41 ± 6, and 31 ± 5% under dry conditions (<1% RH), increasing to 57 ± 9, 53 ± 8, and 41 ± 12% under humid conditions, respectively (Table 2). For 1-hexene and 1-octene, our dry values are lower but in reasonable agreement with results obtained at 3−5% RH by Atkinson et al.[66] and Grosjean et al.,[64,65] which fell in the range 47−54% (Table 2); a fraction of the difference may be due to the difference in RHs. In another study in our laboratory, we found an even larger dependence on RH, measuring 38 ± 3% under dry conditions (<1%) rising to 66 ± 6% at high humidity (80%).[26] Our nonanal yields are somewhat lower than the other alkenes and that measured by Grosjean et al.,[64] 49 ± 12% at 3−7% RH. Like nonanoic acid, nonanal may also have been subject to some losses.

(3.2) Internal Alkenes: *trans*-3-Octene and 1-Methylcyclohexene. Pentanoic acid yields from *trans*-3-octene are 5.0 ± 1.5 and 2.8 ± 0.8% under dry and humid conditions, respectively (Table 2, Figure 2). As for other alkenes, the acid yield drops (by 44%) under humid conditions. Carbonyl yields (Table 2 and Figure 2) are as follows: propanal, 50 ± 8 (dry) and 62 ± 19% (humid); pentanal, 48 ± 7 (dry) and 61 ± 9% (humid). No literature data for acids and carbonyl yields for *trans*-3-octene are available.

1-Methylcyclohexene ozonolysis experiments (one experiment at each humidity) were carried out in the 240 L chamber; thus, only end-point sampling was performed, and no information about the linearity of product yield curves was obtained. The production of 6-oxoheptanoic acid is found to be 0.7% under both dry and humid conditions (Table 2). 6-Oxoheptanoic acid is expected from direct rearrangement of the 6-oxo-CIs formed in 1-methylcyclohexene ozonolysis (Figure 3). The other initial decomposition isomer, a 7-oxy-2-carbonyl oxide, cannot form an acid directly.

We detected several additional oxygenated mono- and dicarboxylic acids, including hexanedioic, pentanedioic, 5-oxohexanoic, and, tentatively, 6-hydroxyhexanoic and 5-hydroxypentanoic acids with yields of 1.6, 1.4, 1.9, 0.7, and 0.6%, respectively, independent of humidity. The mass spectra of the doubly derivatized hydroxy acids provided excellent matches to the NIST library spectra; however, the identifications were not verified by other methods. The total yield of C_5 and larger acids was about 7%. In conjunction with the study described in the companion paper in this issue[40] we also determined formation of formic and acetic acids from 1-methylcyclohexene ozonolysis using solid-phase microextraction (SPME). Yields were 12 ± 2 and 6.5 ± 3%, respectively.

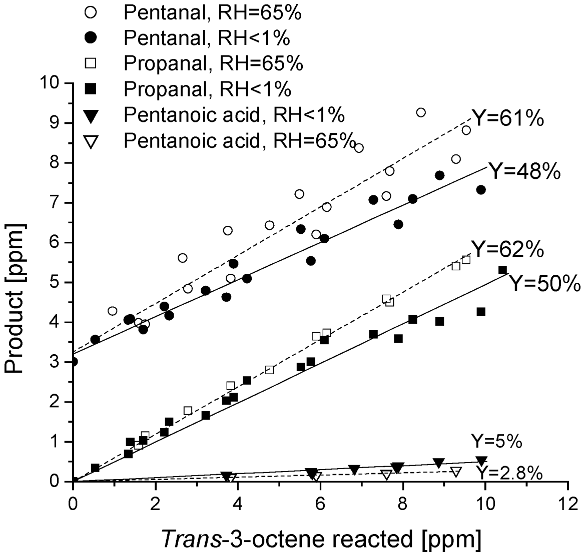


Figure 2. Heptanoic acid from 1-octene ozonolysis under dry (filled circles) and humid (open circles) conditions and selected experiments with added SCI scavengers.

Literature specifically investigating methylcyclohexene is limited to one investigation, but α-pinene, which is structurally similar, has been studied repeatedly (Table 2). A handful of studies of cyclohexane have also been carried out (Table 2). Analogues of the acids observed here, with the exception of the specific isomers of the hydroxy acids, have been observed in each of the other systems. The acid that may be formed directly, 6-oxoheptanoic acid, has as analogues pinonic acid from α-pinene and 6-oxohexanoic acid from cyclohexane. Similarly, hexanedioic acid has as analogues pinic and pentanedioic acids. 5-Oxohexanoic acid is an analogue of norpinonic acid and 5-oxopentanoic acid, and finally pentanedioic acid is an analogue of norpinic and butanedioic (succinic) acids from α-pinene and cyclohexene, respectively. Yields reported in the literature vary widely (Table 2). The early observation by Christoffersen et al.[33] that pinic acid production was highly dependent on the precursor concentrations has not been borne out by subsequent studies; results appear to be more method-dependent. In general the results from Seinfeld and co-workers,[35,37] performed with PFBHA derivatization, found the highest yields, by a factor of 5−20 compared to most other studies (Table 2). Their initial concentrations were low, in the 50−100 ppb range. The recent Fick et al.[36] results, obtained at even lower concentrations (20 ppb) and with PFBHA derivatization but downstream of an O_3 scrubber found yields that are lower than Seinfeld and co-workers results by about a factor of 10. Koch et al.[4] used BF_3 to generate methyl esters from acids collected on filters and, using higher initial concentrations (∼3 ppm), found yields that fell in the lower midrange. Also in the lower midrange are results of Glasius et al.,[32] who used LC-MS without derivatization to monitor particulate organic acids. Kalberer et al.,[37] Yu et al.,[35] and Fick et al.[36] all used impingers to monitor acids; the Glasius et al.[32] and Koch et al.[4] work is based on filter collection. The variability highlights the potential for several types of sampling artifacts. Reactions

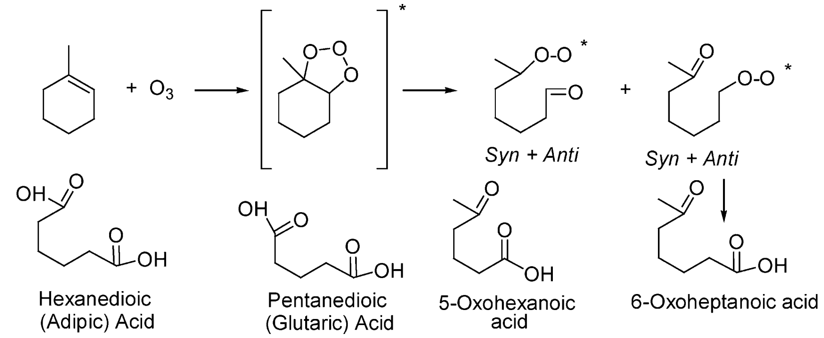


Figure 3. Hexanoic acid and hexanal from 1-octene ozonolysis under dry (filled circles) and humid (open circles) conditions and selected experiments with added SCI scavengers. For clarity, data from experiments with methanol (asterisks) are offset by 0.02; all other data have been offset by 0.05.

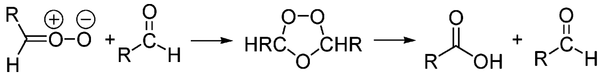
of O_3 with trapped compounds is a potential source of error; however, most studies use alkene in excess, and added O_3 in small aliquots, so that O_3 was completely consumed before sampling; thus, this is not likely a major problem. Filters take up and/or loose variable amounts of gas-phase organic acids. Concentration-dependent chemistry is possible, and likewise losses are more problematic for low-concentration systems. Ozone scrubbers have the potential to remove some particles[32] and, with them, organic acids. Finally, Ziemann[38] pointed out that species in the particles, such as hemiacetals, could be expected to appear as acids in derivatization analyses. Ziemann[38] postulates that some of the observed particle-phase carboxylic acids are decomposition products of peroxyhemiacetals, which are formed in a reaction chain beginning with stabilized Criegee intermediates via hydroperoxides and aldehydes; this may explain some of the discrepancies. In our study we have focused on species that form little if any aerosol in an attempt to avoid the artifacts that may arise from decomposition of particle phase species. Methylcyclohexene does generate some aerosol,[67] however, so our yields for methylcyclohexene may be somewhat elevated if particle-phase hemiacetals appear as acids. On the other hand, we have not verified collection of aerosols in our impinger-based sample train; thus, we may have less than complete recovery of acids that partition strongly into the aerosol phase, such as dicarboxylic acids.

When compared to our measurements, Koch et al.[4] found much lower yields for pentane dioic and 5-oxopentanoic (<2% combined) and formic and acetic acids (0.6%), collected only on filters. In contrast, our results for hexanedioic (1.6%) and 6-oxoheptanoic acids (0.7%) are in remarkably good agreement with the results of Koch et al.,[4] 1.9 and 0.7%, respectively (Table 2), possibly indicating that we are recovering less volatile acids in aerosols, and these partition effectively onto the filters and are therefore well-sampled by Koch et al.[4] Our results are much lower than the results for cyclohexene-derived homologues reported by Kalberer[37] (pentanedioic at 5.9% and 6-oxohexanoic at 4.2%), but our results are similar to the α-pinene results for pinic and pinonic acids measured in the same study. Hatakeyama and co-workers[68,69] investigated organic acids from unsubstituted cycloalkenes and found similar yields as this study for formic acid (~12%) and much higher oxo- and diacid yields, up to 10%; however, the acid yields showed strong secondary behavior, likely due to the small reaction vessel and long reaction times (days).

Fick et al.,[36] investigated the effect of RH on formation yields of acids and other products in α-pinene ozonolysis, finding that the yield of pinonic acid dropped as the RH increased, while the other acids were unaffected. While this result is certainly consistent with our results for all other alkenes and other primary acid products we have studied, in our limited set of experiments, we did not observe a decrease in acid formation for methylcyclohexene.

(3.3) Formation of C_{N-1} and C_{N-2} Acids. Pinic acid from α-pinene is a diacid that has lost one carbon atom from its backbone. Analogous acids are observed from all cyclic alkenes studied (above). In this work, we have identified the analogues from terminal linear alkenes, which because one C breaks away in the initial ozonolysis step, have a C_{N-2} backbone (i.e. hexanoic acid from 1-octene). Mechanisms for formation of these acids (from cycloalkenes) that have been proposed in the literature require cyclic transition states that involve the carbonyl or organic acid on the other end of the broken ring;[4,19,35,68] however, it is unlikely that C_{N-2} acids from linear alkenes also arise via a cyclic transition state. Further, since the yields of C_{N-2} are independent of RH, they do not appear to arise from SCI reaction with water. Addition of other SCI scavengers suppresses hexanoic acid, however, which implies they may be a product of SCI chemistry.

(3.4) SCI Scavenger Experiments. To further investigate the pathway for acid formation, we performed a series of 1-octene ozonolysis experiments under dry conditions with added SCI scavengers: propanal, hexafluoroacetone (HFA), and methanol. Scavenger concentrations (Table 3) were chosen such that most or all SCI would be scavenged prior to decomposition or reaction with acids or aldehydes from the primary ozonolysis (above). In all of the SCI scavenger experiments, cyclohexane was added in large excess; thus cyclohexane, rather than the SCI scavenger, still scavenged almost all OH (at least 76% but in most cases more than 95%), and thus the HO_2/RO_2 chemistry will have been quite similar among all experiments. Propanal concentrations were chosen on the basis of Fenske et al.[49] experiments in which secondary ozonide formation from the ozone–*trans*-2-butene reaction (R5) leveled off once propanal exceeded calculated SCI levels by a factor of 13:



(R5)

Neeb et al.[70] observed no formation of hydroperoxy methyl formate (HPMF) when added acetaldehyde exceeded SCI from ethene ozonolysis by a factor of 6, finding propene ozonide instead. In the two experiments we performed, propanal was in excess by a factor of 2.3 and 33 compared to calculated SCI levels, respectively. The latter of the two can be expected to have scavenged all SCI.

Neeb et al.[71] found that addition of methanol to ethene ozonolysis resulted in formation of methoxy alkyl hydroperoxides and decreased formation of hydroperoxymethylformate and formic acid anhydride; maximum formation of the new

TABLE 3: Initial Conditions and Product Yields for Experiments with 1-Octene with Added SCI Scavengers[a]

1-octene (ppm)	cyclohexane (ppm)	SCI scavenger (ppm)	heptanoic acid yield (%)	heptanal yield (%)	hexanoic acid yield[b] (%)	hexanal yield (%)
10.7−13	2690−3700	<5% RH	8.3	41	1.8	4.2
10.7−13	2690−3700	65% RH	4.4	53	1.8	4.2
Methanol						
8.16	3620	110	6.1	39	0.9	3.7
11.3	4040	800	3.6	42	0.9	3.3
11.0	3760	7900	3.2	41	ND	1.8
8.54	3360	7900	3.4	43	ND	1.9
Propanal						
12.7	5200	7.3	10.8	39	1.8	3.3
11.7	4920	95.9	10.0	42	0.6	2.4
HFA[c]						
12.30	4460	3.88	21.4	61	1.0	2.1
12.3	4300	4.98	20.7	70	1.0	1.6
12.6	4460	5.27	22.5	54	0.6	2.2

[a] Experiments were performed at less than 1% RH and with cyclohexane to scavenge OH. [b] ND, not detected. [c] Hexafluoroacetone.

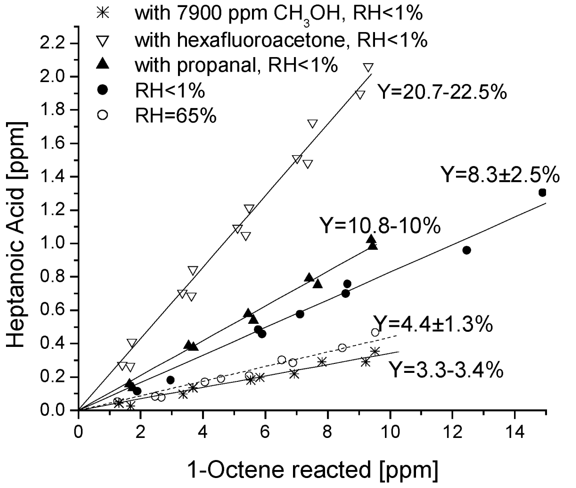


Figure 4. Formation yields of products from *trans*-3-octene ozonolysis under dry (filled symbols) and humid (open symbols) conditions.

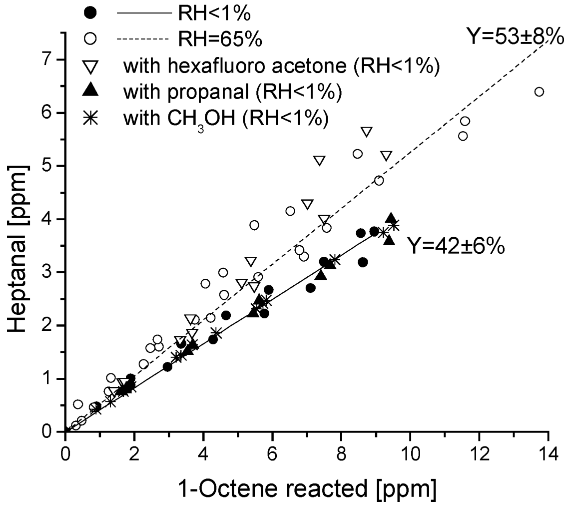


Figure 5. Pathway leading to the production of 6-oxoheptanoic acid and structures of other acids generated in ozonolysis of methylcyclohexene.

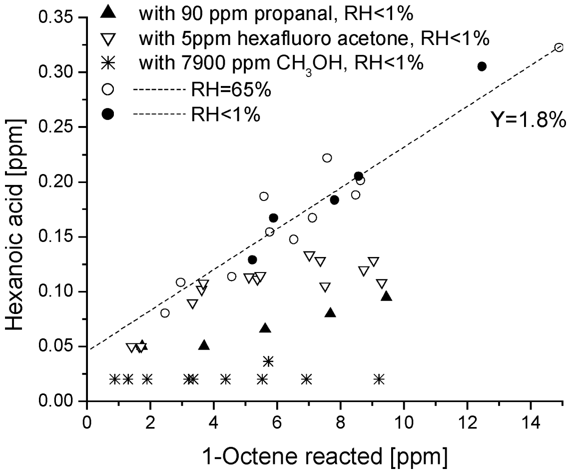
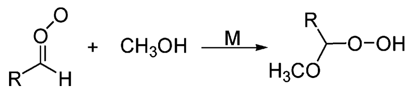


Figure 6. Heptanal from 1-octene ozonolysis under dry (filled circles) and humid (open circles) conditions and selected experiments with added SCI scavengers.

product occurred once methanol exceeded the initial ethene concentration by a factor of 10:



$$\mathrm{RCH{=}O^{+}{-}O^{-}} + \mathrm{CH_3OH} \xrightarrow{M} \mathrm{R(H_3CO)CH{-}O{-}OH}$$

(R6)

We added methanol in excess of the initial octene concentration by factors of ~20−1300, and of SCI formed by factors of 55, 290, 2900, and 3800. The two lower concentrations did not appear to completely scavenge all SCIs, while the higher concentrations did (Table 3).

Horie et al.[52] found that hexafluoroacetone (HFA) reacts more rapidly with the C_1 SCI from ethene ozonolysis than does acetaldehyde, by a factor of 13, thus only small quantities of HFA are required to act as an effective scavenger. Horie et al.[52] however needed to add an amount of HFA about five times that of the SCI produced before the proportion of HFA consumed (relative to alkene reacted) reached a maximum. In our experiments, we added hexafluoroacetone equal to only 1.2−1.7 times the expected quantity of SCI; thus, we may not have scavenged all of the SCI. We did not observe, however, any difference in the product distribution as the HFA concentration was increased over this range.

The results of the scavenger experiments are shown in Table 3 and Figures 4−7. Addition of the carbonyls hexafluoroacetone and propanal resulted in qualitatively similar results. Hexafluoroacetone led to a marked increase (about 2.5 times) in heptanoic acid production relative to experiments conducted under dry conditions and also an increase in formation of heptanal (about 1.5 times), although the latter appeared to be due partly to a secondary source, as indicated by the slight nonlinearity of its yield curve. Formation of hexanal and hexanoic acid, in contrast,

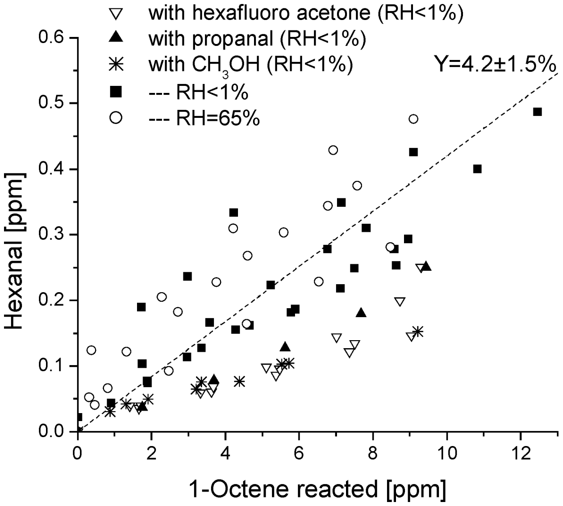


Figure 7. Hexanal from 1-octene ozonolysis under dry (filled circles) and humid (open circles) conditions and selected experiments with added SCI scavengers.

were reduced. Addition of excess propanal also increased heptanoic acid yields, but only slightly, from 8.3 to 10%. Methanol, in contrast, reduced heptanoic acid formation by about 60%, relative to experiments at RH < 1% without added scavenger. This result is in reasonable agreement with Docherty et al.[53] who report that acid yields for ozonolysis of somewhat larger alkenes (decene to tridecene) with excess methanol were in the range of 1−2.5%. Heptanal was unchanged within uncertainties, hexanal was reduced by a factor of 2, and hexanoic acid was reduced almost to zero. Addition of more modest quantities of methanol reduced the heptanoic acid by a smaller degree and had a smaller impact on hexanoic acid and hexanal.

The observation that hexafluoroacetone and propanal both increase acid formation is consistent with the notion that carbonyls add to SCIs and partially decompose to acids (R5).[71] Hexafluoroacetone appears to be more efficient at generating acids than propanal, for reasons that are unknown. Interestingly, the sum of heptanoic acid and additional heptanal in the hexafluoroacetone experiments is roughly equal to the SCI yield from 1-octene ozonolysis of 36% measured by Hasson et al.[26]

Water and methanol reacting with SCI both produce oxyhydroperoxides; specifically hydroxyhydroperoxides (R4) and methoxyhydroperoxides (R7),[31,38,53] respectively. Methoxyhydroperoxides appear to dehydrate to methyl esters.[53] Generation of acids from oxyhydroperoxides (R4c,d), while predicted by quantum chemical calculations, has not thus far been borne out by indirect experimental evidence (above). Addition of methanol inhibits acid formation somewhat more than water, reducing the heptanoic acid yield to 3.4 vs 4.4%, respectively, suggesting that most if not all of the acid observed in high-humidity experiments is formed directly (R3) and not via reactions R4c or R4d.

The SCI scavengers hexafluoroacetone, propanal, and methanol substantially inhibited hexanoic acid and hexanal production. In contrast, hexanal and hexanoic acid formation was unaffected by humidity. Hexanal is an expected byproduct of the OH channel from *syn*-carbonyl oxides; however, a direct source of hexanoic acid is not known.

(3.5) Pathways to Acid Formation. Production of primary acids (i.e. those that can arise from rearrangement of a primary carbonyl oxide) from alkene ozonolysis in all cases studied, including the small alkenes in the preceding paper in this issue[40] decrease at high humidity, by 37 ± 13%. While the decrease in acid yield with increasing humidity is fairly variable, there is no particular trend based on structure.

There are several possible interpretations of this result, the simplest of which are as follows: (1) that about 60% of acids observed under dry conditions and persisting under humid conditions are not derived from SCI reactions, but rather from direct rearrangement and stabilization of presumably *anti*-carbonyl oxides (R3a−d, and thus persist in the presence of SCI scavengers—in this case, water). The other 40% arises from SCI reactions with aldehydes, with acids, or via rearrangement, which are the fates of SCIs under dry conditions. Thus, under humid conditions, water reacts with SCI generating no acids, leaving the 60% of acids observed under dry conditions that are formed directly. (2) An alternative explanation is that the water reaction with SCI may be responsible for all or a portion of acids generated under humid conditions, but it is somewhat less efficient than the reactions that take over under dry conditions. This interpretation provides an upper limit for acid production from the water−SCI reaction (R4) via a combination of the OH production channel (R4d) and rearrangement (R4c) of 20% of (R4) for 1-octene; 20% is arrived at by dividing observed humid acid yield (4.4%, this study) by the yield of C_7−SCI from octene ozonolysis (about 22%).[26,53] (3) The third possible pathway is via R3a−e, whereby an *anti*-carbonyl oxide decomposes to generate OH and an acyl radical, which will add O_2 to form an acylperoxy radical, and can in turn react with HO_2 to form an acid.

In addition to the attractive simplicity of the direct formation hypothesis, additional observations are suggestive that this hypothesis is correct. (i) That addition of a large excess of methanol does not shut off the acid production entirely supports the first hypothesis, although the fact that the acid yield is depressed somewhat below the humid acid yield lends some credence to a small acid yield from the water−SCI reaction (R4c,d). (ii) The observation that primary acid yields from smaller alkenes and cyclic alkenes are much smaller than those from larger or terminal alkenes is consistent with the notion that a step involving stabilization exerts some control over acid formation, more consistent with hypothesis 1. The energy partitioning in the decomposing of primary ozonides (R1) depends on the number of available vibrational modes, which increases rapidly as carbon atoms are added to the molecule.[43,72] For C_4, C_5, and C_8 terminal alkenes RRK calculations performed by Holbrook et al.[73] showed that when the size of a primary ozonide increases, the lowest energy pathway becomes favored and the yield of *anti*-carbonyl oxides increases at the expense of *syn*-carbonyl oxides. Hypothesis 3, formation of acids after generation of OH by *anti*-carbonyl oxides, can likely only account for a small amount of acid. For example, to account for the 5% acid yield observed under wet conditions the following conditions would have to be met: The OH from 1-octene, a 10% yield, would need to be generated entirely from the *anti*-carbonyl oxide rather than *syn* (R2, very unlikely[26]); all of the cogenerated acyl radicals would have to, once converted to acylperoxy radicals, react with HO_2 rather than RO_2, (not possible given the OH scavenger chemistry in our experiments); and the yield of acid from the HO_2 reaction would need to be at 50%, the upper limit of its uncertainty range.[48] Additionally, hypothesis 3 would suggest that acid yields would correlate positively with OH yields for different alkenes, which they do not.

(3.6) Effect of Added OH Scavenger. Several studies have investigated the effect of OH scavengers on acid yields, with varying results. Fick et al.[36] observed dramatic reductions of acid formation when scavengers were added. Glasius et al.[32] also observed lower acid yields for all identified acid products in the presence of an OH scavenger (methylcyclohexane), but only by factors of 1.5−2. These results are in excellent agreement with the work of Koch et al.,[4] who also observed a decrease of acids, also by factors of 1.5−2 upon addition of cyclohexane. On the other hand, Yu et al.[35] saw almost no effect of scavengers on acid yields. Our experiments do not corroborate the disappearance of acids in the absence of OH chemistry, although higher acid yields in the absence of scavengers do seem likely because organic acid formation from aldehydes reacting with OH in the presence of HO_2 can be very high (unpublished work, this laboratory). Because the OH-derived acid formation chemistry is HO_2-dependent, however, it can be expected to be sensitive to other factors, such as the particular scavenger chosen.

(3.7) Atmospheric Implications. Under most conditions in the atmosphere, SCIs are expected to primarily react with water or undergo unimolecular decomposition, although in some locations, reactions with SO_2, or possibly NO_2, may also compete.[49] Reactions with aldehydes and organic acids, while important in most higher concentration laboratory experiments, are too slow to compete in ambient air.[49]

Data on acid formation from ozonolysis of C_3 and alkenes uniformly indicate that acid formation is modest; less than 9% under dry conditions and less than 5% under humid conditions. In this study, we have focused on the effect of relative humidity, and our results indicate that acid formation drops markedly in the presence of water vapor. Earlier studies in this laboratory indicate that the transition RH below which stabilized CI mostly decompose or react with compounds other than water occurs between 15 and 40% RH, depending on the alkene.[25,26] The transition between low and high RH is likely most sensitive to the decomposition rate of the SCI. However, because interference from some SCI reaction partners, such as aldehydes, takes place in our experiments but not in the atmosphere, the water reaction dominates at somewhat lower RHs in the atmosphere. Thus, under most conditions in the atmosphere, the lower yields (below 5%) observed at higher humidities apply. Since modeling studies have typically assumed that acid yields from alkene ozonolysis were the same as that for ethene, 40%; this work indicates this source of acids has been overestimated by a factor of about 10 and points to the importance of other sources of organic acids in the atmosphere: primary emissions and reactions of aldehydes in the presence of HO_2.

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References and Notes

(1) Kawamura, K.; Kasukabe, H.; Barrie, L. *Atmos. Environ.* **1996**, *30*, 1709.

(2) Fraser, M. P.; Cass, G. R.; Simonet, B. R. T. *Environ. Sci. Technol.* **2003**, *31*, 2356.

(3) Pio, C.; Alves, C.; Duarte, A. *Atmos. Environ.* **2001**, *35*, 389.

(4) Koch, S.; Winterhalter, R.; Uherek, E.; Kollof, A.; Neeb, P.; Moortgat, G. K. *Atmos. Environ.* **2000**, *34*, 4031.

(5) Kawamura, K.; Steinberg, S.; Kaplan, I. *Atmos. Environ.* **2000**, *34*, 4175.

(6) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simonet, B. R. T. *Environ. Sci. Technol.* **2002**, *36*, 1169.

(7) Servant, J.; Kouadio, G.; Cros, B.; Delmas, R. *J. Atmos. Chem.* **1991**, *12*, 367.

(8) Yu, J.; Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. *Geophys. Res. Lett.* **1999**, *26*, 1145.

(9) Lefer, B. L.; Talbot, R. W.; Harriss, R. C.; Bradshaw, J. D.; Sandholm, S. T.; Klemm, K. I.; Gorzelska, K.; Barrick, J. *J. Geophys. Res., [Atmos.]* **1994**, *99*, 1721.

(10) Herron, J. T.; Huie, R. E. *Int. J. Chem. Kinet.* **1978**, *10*, 1019.

(11) Madronich, S.; Chatfield, R. B.; Calvert, J. G.; Moortgat, G., K.; Veyret, B.; Lesclaux, R. *Geophys. Res. Lett.* **1990**, *17*, 2361.

(12) Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233.

(13) Whelpdale, D. M.; Summers, P. W.; Sanhueza, E. *Environ. Monitor. Assess.* **1997**, *48*, 217.

(14) Khare, P.; Kumar, N.; Kumari, K. M.; Srvastava, S. S. *Rev. Geophys.* **1999**, *37*, 227.

(15) Calvert, J. G.; Stockwell, W. R. *Environ. Sci. Technol.* **1983**, *17*, 428A.

(16) Jacob, D. J.; Wofsy, S. C. *J. Geophys. Res., [Atmos.]* **1988**, *93*, 1477.

(17) Grosjean, D. *Environ. Sci. Technol.* **1989**, *23*, 1506.

(18) Pun, B. K.; Seigneur, C.; Grosjean, D.; Saxena, P. *J. Atmos. Chem.* **2000**, *35*, 199.

(19) Jenkin, M. E.; Shallcross, D. E.; Harvey, J. N. *Atmos. Environ.* **2000**, *34*, 2837.

(20) Calvert, J. G.; Su, F.; Bottenheim, J. W.; Strausz, O. P. *Atmos. Environ.* **1978**, *12*, 197.

(21) Hatakeyama, S.; Bandow, H.; Okuda, M.; Akimoto, H. *J. Phys. Chem.* **1981**, *85*, 2249.

(22) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437.

(23) Anglada, J. M.; Aplincourt, P.; Bofill, J. M.; Cremer, D. *ChemPhysChem* **2002**, *2*, 215.

(24) Winterhalter, R.; Neeb, P.; Grossmann, D.; Kolloff, A.; Horie, O.; Moortgat, G. *J. Atmos. Chem.* **1999**, *35*, 165.

(25) Hasson, A. S.; Orzechowska, G. E.; Paulson, S. E. *J. Geophys. Res., [Atmos.]* **2001**, *106*, 34131.

(26) Hasson, A. S.; Ho, A. W.; Kuwata, K. T.; Paulson, S. E. *J. Geophys. Res., [Atmos.]* **2001**, *106*, 34143.

(27) Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1991**, *25A*, 1881.

(28) Horie, O.; Neeb, P.; Moortgat, G. K. *Int. J. Chem. Kinet.* **1997**, *29*, 461.

(29) Su, F.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1980**, *84*, 239.

(30) Sauer, F.; Schafer, C.; Neeb, P.; Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1999**, *33*, 229.

(31) Neeb, P.; Sauer, F.; Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1997**, *31*, 1417.

(32) Glasius, M.; Lahaniati, M.; Calogirou, A.; Di Bella, D.; Jensen, N. R.; Hjorth, J.; Kotzias, D.; Larsen, B. R. *Environ. Sci. Technol.* **2000**, *34*, 1001.

(33) Christoffersen, T. S.; Hjorth, J.; Horie, O.; Jensen, N. R.; Kotzias, D.; Molander, L. L.; Neeb, P.; Ruppert, L.; Winterhalter, r.; Virkkula, A.; Writz, K.; Larsen, B. R. *Atmos. Environ.* **1998**, *32*, 1657.

(34) Jang, M.; Kamens, R. M. *Atmos. Environ.* **1999**, *33*, 459.

(35) Yu, J.; Cocker, D. R., III; Griffin, R. J.; Flagan, R. C.; Seinfeld, J. H.; Blanchard, P. *J. Atmos. Chem.* **1999**, *34*, 207.

(36) Fick, J.; Pommer, L.; Nilsson, C.; Andersson, B. *Atmos. Environ.* **2003**, *37*, 4087.

(37) Kalberer, M.; Yu, J.; Cocker, D.; Flagan, R.; Seinfeld, J. *Environ. Sci. Technol.* **2000**, *34*, 4894.

(38) Ziemann, P. J. *J. Phys. Chem. A* **2002**, *106*, 4390.

(39) Docherty, K.; Ziemann, P. *J. Chromatogr., A* **2001**, *921*, 265.

(40) Orzechowska, G. E.; Paulson, S. E. *J. Phys. Chem. A* **2005**, *109*, 5358.

(41) Bach, R.; Owensby, A.; Andres, J.; Schlegel, H. *J. Am. Chem. Soc.* **1992**, *114*, 7207.

(42) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(43) Paulson, S. E.; Chung, M. Y.; Hasson, A. S. *J. Phys. Chem. A* **1999**, *41*, 8125.

(44) Orzechowska, G. E.; Paulson, S. E. *Atmos. Environ.* **2001**, *36*, 571.

(45) Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.* **1998**, *292*, 97.

(46) Donahue, N. M.; Kroll, J. H.; Anderson, J. G.; Demerjian, K. L. *Geophys. Res. Lett.* **1998**, *25*, 59.

(47) Fenske, J. D.; Kuwata, K. T.; Houk, K. N.; Paulson, S. E. *J. Phys. Chem. A* **2000**, *104*, 7246.

(48) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmos. Environ.* **1992**, *26A*, 1805.

(49) Fenske, J. D.; Hasson, A. S.; Ho, A. W., Paulson, S. E. *J. Phys. Chem. A* **2000**, *104*, 9921.

(50) Hatakeyama, S.; Akimoto, H. *Res. Chem. Intermed.* **1994**, *20*, 503.

(51) Rickard, A. R.; Johnston, D.; McGill, C. D.; Marston, G. *J. Phys. Chem. A* **1999**, *103*, 7556.

(52) Horie, O.; Schafer, C.; Moortgat, G. K. *Int. J. Chem. Kinet.* **1999**, *31*, 261.

(53) Docherty, K. S.; Kumboonlert, K.; Lee, I. J.; Ziemann, P. J. *J. Chromatog., A* **2004**, *1029*, 205.

(54) Crehuet, R.; Anglada, J. M.; Bofill, J. M. *Chem.−Eur. J.* **2001**, *7*, 2227.

(55) Aschmann, S. M.; Atkinson, R.; Arey, J. *Atmos. Environ.* **2002**, *36*, 4347.

(56) Hasson, A. S.; Chung, M. Y.; Kuwata, K. T.; Converse, A.; Paulson, S. E. *J. Phys. Chem. A* **2003**, *107*, 6176.

(57) Ryzhkov, A. B.; Ariya, P. A. *Chem. Phys. Lett.* **2003**, *367*, 423.

(58) Scanlon, J. T.; Willis, D. E. *J. Chromatogr. Sci.* **1985**, 333.

(59) Orzechowska, G. E. Atmospheric Chemistry of Ozone Reactions with Alkenes. Ph.D., University of California, Los Angeles, CA, 2003.

(60) Baker, J.; Aschmann, S. M.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2002**, *34*, 73.

(61) Paulson, S. E.; Seinfeld, J. H. *J. Geophys. Res.* **1992**, *97*, 20703.

(62) Paulson, S. E.; Seinfeld, J. H. *Environ. Sci. Technol.* **1992**, *26*, 1165.

(63) Tobias, H. J.; Docherty, K. S.; Beving, D. E.; Ziemann, P. J. *Environ. Sci. Technol.* **2000**, *34*, 2116.

(64) Grosjean, D., E.; Grosjean; Seinfeld, J. H. *Environ. Sci. Technol.* **1996**, *30*, 1038.

(65) Grosjean, E.; Grosjean, D. *Environ. Sci. Technol.* **1996**, *30*, 2036.

(66) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Envir. Sci. Technol.* **1995**, *29*, 1860.

(67) Wang, S. C.; Paulson, S. E.; Grosjean, D.; Flagan, R. C.; Seinfeld, J. H. *Atmos. Environ.* **1991**, *26A*, 403.

(68) Hatakeyama, S.; Tanonaka, T.; Weng, J.; Bandow, H.; Takagi, H.; Akimoto, H. *Environ. Sci. Technol.* **1985**, *19*, 935.

(69) Hatakeyama, S.; Ohno, M.; Weng, J.; Takagi, H.; Akimoto, H. *Environ. Sci. Technol.* **1987**, *21*, 52.

(70) Neeb, P.; Horie, O.; Moortgat, G. K. *Tetrahedron Lett.* **1996**, *37*, 9297.

(71) Neeb, P.; Horie, O.; Moortgat, G. K. *Int. J. Chem. Kinet.* **1996**, *28*, 721.

(72) Olzmann, M.; Kraka, E.; Cremer, D.; Gutbrod, R.; Schindler, R. *J. Phys. Chem. A* **1997**, *101*, 9421.

(73) Holbrook, K. A.; Piling, M. J.; Robertson, S. H. *Unimolecular Reactions*; Wiley: New York, 1996.