Photochemical Sources of Organic Acids. 1. Reaction of Ozone with Isoprene, Propene, and 2-Butenes under Dry and Humid Conditions Using SPME

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Formation of C_4 and smaller carboxylic acids from gas-phase ozonolysis of several alkenes under dry (relative humidity (RH) < 1%) and humid (RH = 65%) conditions have been investigated. We have developed a technique based on solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) to quantify the acids, as well as other products, and applied it to the reactions of ozone with propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene. Acetic acid yields from propene and *trans*-2-butene ozonolysis in the presence of an OH scavenger were 2.7 ± 0.6 and 2.9 ± 0.6%, respectively, under dry conditions and 1.8 ± 0.4 and 2.3 ± 0.5% at 65% RH. Isoprene ozonolysis produced methacrylic and propenoic acids with yields of 5.5 ± 1 and 3.0 ± 1%, under dry conditions and 4.1 ± 1 and 1.5 ± 0.3% under wet conditions, respectively. That water inhibits acid formation indicates that the water reaction with stabilized Criegee intermediates is at most a minor source of acids. Acids that may form as coproducts of the OH radical elimination pathway, acetic acid from 2,3-dimethylbutene and isoprene, and propenoic acid from isoprene were also observed with significant yields (up to 10%), although the production of acetic acid was not a linear function of the alkene reacted. Carbonyl products are also reported.

1. Introduction

Organic acids are ubiquitous, in the gas phase and in clouds, rain, and aerosols. For example, Keene et al.[1] estimated that formic acid and acetic acids contribute 25−98% of the volume weighted free acidity in precipitation in remote regions of the world. Straight-chain C_1-C_9 monocarboxylic, C_2-C_6 dicarboxylic, and several aromatic acids have been detected in gas, rain, and aerosol samples collected at urban, rural, and remote sites.[2−4] Several possible sources have been suggested for organic acids in the atmosphere. The largest of these are direct emissions from anthropogenic,[5] biogenic,[6] and biomass burning sources[7] and homogeneous oxidation of hydrocarbons.[8,9] The relative contribution of each of the sources is debated and is likely dependent on location.[10−12] The recent recognition nucleation and growth of secondary organic aerosols as substantially enhanced by inorganic acids has recently been extended to include organic acids.[13]

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.[10,14−17] The ozone−alkene source has been thought to arise from the reaction of a so-called stabilized Criegee intermediate (SCI) reacting with water[18−20] and is largely based on extrapolation of results for ethene ozonolysis. Recent quantum chemical calculations by Anglada and co-workers[21] further support the notion that acids should be a major product of the reaction of the stabilized Criegee intermediate, generated in alkene ozonolysis, with water. However, recent experimental 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 hydropeoxides (H_2O_2 and/or organic hydroperoxides) instead.[21−23]

Organic acid production from O_3 reactions with alkenes was observed as early as 1972 by O'Neal and Blumstein.[22] Since then, a number of studies have focused on formation of formic acid from ethene, propene, and *trans*-2-butene[8,23−25] and are in reasonable agreement with one another. A few studies have considered acetic acid from propene and *trans*-2-butene[8,26,27] and aerosol phase acids from terpenes and terpene analogues such as methylcyclohexene (see ref 28). Formation of acids larger than formic from isoprene ozonolysis has been observed but not quantified by Chien et al.[29] and Sauer et al.[25] For C_2 and larger acids for which there are more than one or two measurements in the literature, yields vary by more than an order of magnitude.

Here, we investigate formation of carboxylic acids C_2 and larger from the ozone reaction with the following alkenes: ethene, propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene (2-methyl-1,3-butadiene). This is the first quantitative study of the formation of higher acids from isoprene and the first systematic study of the effect of humidity on acid formation. We also monitored formic acid; however, we believe that the majority of the formic acid was the result of heterogeneous reactions of other species during solid-phase microextraction sampling.[30]

The first four alkenes have primarily anthropogenic sources. Ethene and propene can be quite abundant in urban air, with concentrations of the order of 4 and 1% of the total volatile organic carbon, respectively, and concentrations of several parts per billion (ppb). Outside of urban areas their concentrations are generally lower, but they are sufficiently abundant that they are observable at parts per trillion (ppt) levels around the globe.[31,32] Because of their reactivity, internal alkenes are generally at mid pptC to low ppbC levels in ambient air;[33] however, because their rate constants for reaction with ozone are so much higher than the terminal alkenes ethene and propene, internal alkenes are frequently responsible for the majority of reactivity via this pathway. Isoprene is the most significant biogenic

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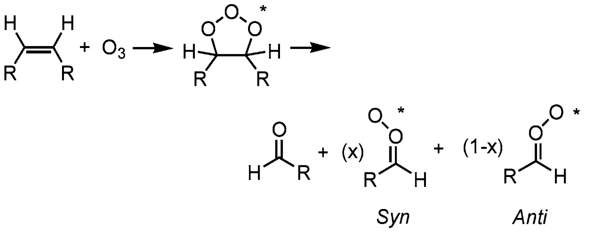
hydrocarbon in the troposphere; it is emitted from a wide variety of mostly deciduous vegetation, and ambient concentrations typically fall in the mid ppt to low ppb range.[31]

Solid phase microextraction (SPME) has been used successfully to sample organic acids in aqueous environmental and biomedical samples. Several techniques have been developed for analysis of C_2–C_8 acids; some proceed by adding derivatization agents directly to the aqueous sample and then sampling the derivatized acid onto the SPME fiber.[34] Others use direct adsorption of the acids from either the aqueous sample[35] or the headspace after acidification of the solution to partition the acids efficiently into the gas phase.[36] Finally, two studies have used derivatization agents, external to the sample, either by depositing them on the fiber or by sampling them simultaneously with the acids.[37] Here, we have developed a method for in-situ monitoring of gas-phase C_1 to C_4 acids using SPME.

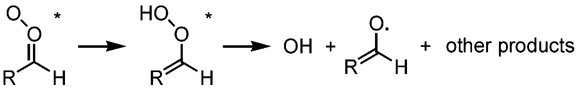
2. Alkene Ozonolysis

It is generally accepted that the reaction of ozone with alkenes is initiated with a 1,3 cycloaddition across the double bond to form a primary ozonide, followed by a concerted cycloreversion to produce a carbonyl compound and a so-called Criegee intermediate (R1). On the basis of structural calculations,[38] the nascent Criegee intermediate is believed to adopt the carbonyl oxide structure shown below, rather than the isomeric dioxirane or bis-oxy forms:



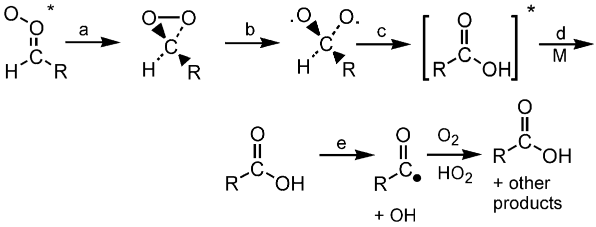
(R1)

Reaction R1 is highly exothermic, resulting in the release of ~60 kcal mol^{-1} into the reaction products;[39] thus a number of unimolecular isomerization and decomposition channels are thermodynamically accessible to the carbonyl oxides (R2, R3). The most important decomposition pathway for syn carbonyl oxides produces OH radicals. OH radical yields from ethene, propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene investigated here are ~18, 35, 64, 67, and 25%.[40–42]



(R2)

The lowest barrier available to *anti*-carbonyl oxides is isomerization to dioxirane, at about 20 kcal/mol.[43] This pathway may lead to acid production (R3), as was first proposed by O'Neal and Blumstein.[22] Since this early study, a series of ab initio and quantum chemical studies have investigated the process.[43,44] 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.[43] 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,[43,45,46] such that generation of the acyl radical should be small. Further, the reaction with HO_2 (R3e) generates acids with a yield of only 20–50%;[47] thus this pathway should be responsible for very small acid yields (<5% and probably less than 1%).

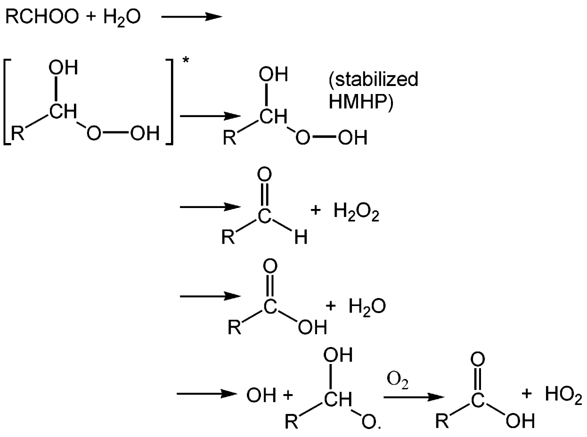


(R3)

A fraction of the nascent CI, likely most of it formed initially as an *anti*-carbonyl oxide,[48] survives long enough to undergo bimolecular reactions. The structure of this species is not known. SCIs have lifetimes with respect to decomposition on the order of milliseconds,[49] on the same time scale as bimolecular reactions. SCIs react with a variety of different compounds, often referred to as Criegee scavengers, including aldehydes, alcohols, carboxylic acids, water, and others.[50] The yield of SCIs can be determined by measuring either the concentration of the unique product or the consumption of the Criegee scavenger in experiments where the scavenger is in "excess". Stabilized Criegee intermediate yields for the alkenes investigated here are ~39, 25, 24, 10, and 27% for ethene, propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene, respectively.[51,52]

The notion that acids are a product of SCIs reacting with water arose in the 1970s. In 1972, Cox and Penkett observed that addition of water suppressed the SCI catalyzed oxidation of SO_2 to sulfuric acid but did not determine the product of the water reaction with SCIs.[53] In their theoretical study of pathways to formation of sulfuric acid in the atmosphere, Calvert et al.[18] speculated that water catalyzes the rearrangement of SCIs to organic acids. Experimental evidence for this was provided in 1981 by Hatakeyama and co-workers,[19] who showed that formic acid formation from peroxymethylene, generated by photolyzing ketene in the presence of O_2, increased as the RH was increased. Peroxymethylene, CH_2OO, has the same formula as the SCI from a terminal alkene; however, it may have a different structure, and it certainly has different energy than that generated from alkene ozonolysis. More recently, Horie and Moortgat[54] showed clearly that peroxymethylene does not have the same chemistry as the SCI generated from ethene ozonolysis. While the notion that SCI + water generates substantial acids was picked up in several modeling studies, there appears to be little experimental evidence for the pathway.

Three channels are thermodynamically accessible for the water reaction, all presumably proceeding through the hydroxy hydroperoxide (HMHP) intermediate:



(R4a)

(R4b)

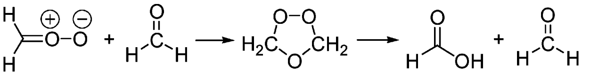
(R4c)

(R4d)

Recently, Anglada and co-workers[21,55] 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). The acid formation pathways are calculated to be 6−11 kcal/mol higher than the aldehyde + H_2O_2 path. However, they conclude that the most facile decomposition pathway for the hydroxyhydroperoxide is RCH(OH)O−OH bond cleavage to produce OH and the $HOCHRO^•$ radical (R4d). $HOCH_2O^•$ and $CH_3CH(O^•)OH$ should rapidly react with O_2 to produce formic or acetic acid and HO_2, respectively; thus, theoretical studies predict high yields of acids from SCI + H_2O.

Two studies have found no dependence of OH formation from alkene ozonolysis on relative humidity (RH), indicating that R4d is at most a minor channel.[56,57] Given their large size, the hydroxyhydroperoxides from terpene ozonolysis studied by Aschmann et al.[56] might be expected to undergo stabilization (R4a); however, this process also seems to be dominant for the smaller ethene and *trans*-2-butene studied by Hasson et al.[57] Interestingly, Ryzhkov and Ariya[58] performed a quantum chemical examination of the reaction of the C_1 SCI with a water dimer (or water with the nascent hydroxymethyl hydroperoxide) and concluded that the main product should be aldehyde + H_2O_2 (R4b), rather than acids (R4c or R4d).

(2.1) Additional Pathways to Formation of Larger Acids. In addition to carboxylic acids produced by the direct pathway (R3) and via reactions of SCI with water (R4c,d), a few other processes can generate acids in ozonolysis experiments. Some acids may arise from the reaction between aldehydes and SCIs, as suggested by Neeb et al.[59] The intermediate may be a secondary ozonide:



(R5)

Because of the dependence on the aldehyde concentration, products of this reaction are expected to exhibit strong secondary behavior, and the reaction should produce only limited quantities of acids. Under dry conditions, the SCI decomposes[49] or reacts rapidly with formic acid, if present, to form hydroperoxy methyl formate (HPMF), limiting the efficacy of this source. Under humid conditions, reaction with water together with decomposition[49] appears to be the primary sink of SCI; thus, the acid contribution from R5 should be small.

Acyl−peroxy radicals produce acids when they react with themselves or with HO_2.[47] Acyl−peroxy radicals result from OH reaction with aldehydes; however, since a sufficient amount of OH scavenger was added (consuming 98% or more OH radicals), this source should result in acid yields of less than 0.2% in the present study. On the other hand, some of the carbonyl oxide decomposition pathways produce acyl-type peroxy radicals, and this is a likely source of C_{N-2} acids, such as acetic acid from isoprene and 2,3-dimethyl-2-butene.

3. Experimental Section

Experiments were carried out at 296 ± 2 K in Teflon chambers (240 L) in the dark and at atmospheric pressure. Alkenes and scavengers were evaporated (liquids) or injected (gases) into the matrix air as the chamber was filled. Alkenes and scavengers (Sigma-Aldrich) had stated purities of 99% or better and were used as received. Experiments performed at RH $< 1\%$ used ultrapure, zero grade cylinder air (Airgas, PA). Humid air was generated by passing purified air (Thermo-Environmental Model 111) through a fritted-glass water bubbler containing deionized water. Humidity in the reaction chamber was measured with a digital hygrometer (Fisher Scientific). Hydrocarbon concentrations were determined using a gas chromatograph/flame ionization detector (GC/FID, Hewlett-Packard 5890), equipped with a capillary column (J&W Scientific, 0.32 mm i.d., 1 μm DB-1 film, 30 m). Samples from the reaction chamber were introduced (on column) via a heated six-port gas-sampling valve (Valco), with the oven programmed to −70 °C for 0.2 min and then 14 °C/min to 200 °C. The GC/FID was calibrated daily with a 4.9 ± 0.1 ppm cyclohexane standard (Scott Gasses). The flame ionization detector (FID) response[60] normalized to the cyclohexane calibration was used to calculate concentrations of hydrocarbons and carbonyl compounds.

After the initial concentrations were established, reactants were allowed to mix and a series of O_3 aliquots were added. Ozone was generated in aliquots by flowing pure O_2 at 0.1 L/min for 12−60 s through a mercury lamp generator (JeLight), in quantities resulting in 0.5−1 ppm in the chamber. After each addition the chamber was mixed manually and allowed to react for 20−30 min and then sampled with the GC/FID and with the SPME device. Experiments lasted 4 h and had average O_3 concentrations of 0.5 ppm or less.

4. SPME

Two fiber coatings were investigated: Carboxen/poly(dimethylsiloxane) (PDMS; 0.85 μm film × 1 cm long) and Carbowax/divinylbenzene (DVB; 70 μm film × 1 cm long) coated on a Stable Flex fiber (Supelco). Carboxen/PDMS is designed for sampling gases and compounds in the molecular weight range of 30−225; Carbowax/DVB is for polar compounds in the molecular weight range of 40−275 (Supelco). The performance of the Carbowax/DVB coating was significantly affected by humidity; thus, its use was discontinued. The Carboxen/PDMS coating has pores ranging from 6 to 50 Å, and extraction of analytes occurs via adsorption. Molecules may also diffuse into the bulk of the coating, resulting in potential carryover. Carryover was completely eliminated by leaving the fiber in the injection port (260 °C) for the entire chromatographic run, typically 12 min. Sample collection was accomplished by inserting the SPME housing through a septum into the Teflon chamber and exposing the fiber for 5 min. Once sampling was complete, the SPME device was withdrawn and inserted in the inlet of the GC/MS for desorption and analysis. Longer sample times result in lower detection limits, but since this was well within our desired concentration range, we chose a shorter sampling time, which resulted in a detection limit of 50 ppb.

Carboxylic acids and other oxygenated hydrocarbons were identified and monitored using a GC/ion trap mass spectrometer (MS, Varian 3800 GC/Saturn 2000 MS). A Stabilwax-DA capillary column (0.32 mm, 1 μm film, 30 m, Restek) was used to separate acids. This column has a poly(ethylene glycol) stationary phase that has been specifically deactivated to analyze acidic compounds. To desorb analytes from the SPME fiber, the GC injector containing a 3.4 mm i.d. deactivated glass liner was held at 260 °C. The split was programmed at 5:1 for 0.1 s, splitless for 1 min, and then split of 100:1 until the end of the run. The initial split was found to improve reproducibility.[30] Analytes were thermally desorbed from the fiber for 1 min in splitless mode and focused on the column, which was held at 40 °C. After 1 min, all remaining sample was ejected from the injector port with a 100:1 split mode, and the GC oven was ramped at 14 °C/min to 200 °C. The transfer line, trap, and manifold temperatures were 200, 100, and 40 °C, respectively.

The MS acquisition program consisted of three segments: a delay segment from 0 to 2 min during which the MS was shut off, followed by a segment from 2 to 5 min to observe products other than acids, and finally a segment during which acids were monitored. The last segment had a multiplier offset of +50 mV to increase sensitivity for acid detection. Compounds were identified using electron-impact (EI) or chemical ionization (CI), and reference spectra were generated from authentic standards.

(4.1) SPME Calibrations. Calibrating gas-phase organic acids and other highly polar compounds, especially at low concentrations, is a difficult undertaking due to strong interactions of these analytes with surfaces. Gas-phase standards of most liquid organic compounds can be prepared using slow diffusion of the desired analyte through a capillary into a dilution stream.[61,62] The capillary assembly and diffusion chamber are maintained at very steady conditions for days to weeks to allow all surfaces to equilibrate.

We constructed a diffusion chamber to generate standards to calibrate formic, acetic, propenoic, and methacrylic acids. A capillary assembly containing cyclohexane, which is independently quantifiable using an FID, was used as an internal standard. Pure liquids were placed in individual capillary assemblies, consisting of a test tube like vial (4 cm × 6 mm o.d. × ~4 mm i.d.) and annealed to a glass capillary tube (12 cm long × 6 mm o.d. × 2 mm i.d.). Compounds diffused from the vial through the capillary and into the diffusion chamber, which was flushed with ultrapure N_2 at a constant flow of 20 mL/min. The diffusion chamber was immersed in a temperature-controlled circulating water bath (Fisher Scientific). The bath was maintained at 25 °C for formic and acetic acids and at 40 °C for methacrylic and propenoic acids. All tubing and connections in the diffusion chamber were constructed from Teflon. The resulting concentration in the diffusion chamber effluent was 3−72 ppm, depending on the volatility of the analyte.

Diffusion rates of acids were determined by mass loss, by removing the capillary assemblies from the diffusion chamber and weighing them every 1−2 weeks.[30] As expected, diffusion rates are inversely proportional to the acid volatility. The mass loss method was independently verified using ion chromatography for formic and acetic acids (Dionex IC, operated by West Coast Analytical Services) and GC/FID analyses for cyclohexane. The mass loss method agreed to within ±2% for the acids and ±1% for cyclohexane.[30] The effluent of the diffusion chamber was used to provide gas standards to construct SPME sampling calibration curves shown in Figure 1 after dilution with zero grade air and humidification as appropriate.[30]

5. Results

(5.1) SPME. Figure 1 shows the calibration curves for formic and acetic acids using samples generated with the diffusion assembly, above. Each data point is an average of 3−10 measurements; error bars show the standard deviation for more than 7 averaged measurements, and the full range of measurements for 7 or fewer points. The calibration data for formic and acetic acid were collected over a period of 8 months with three Carboxen fibers, indicating that the integrity of individual fibers the reproducibility between fibers was better than ±5%. Responses for formic and acetic acids were linear in the target concentration ranges of 100−1500 ppb and 50−600 ppb, respectively. Isolated measurements indicate that the upper end of this linear range could be at least doubled. The lower end of the range can likely also be improved, particularly by increasing the SPME sampling time. The effect of humidity on SPME analysis of the acids was small (Figure 1).

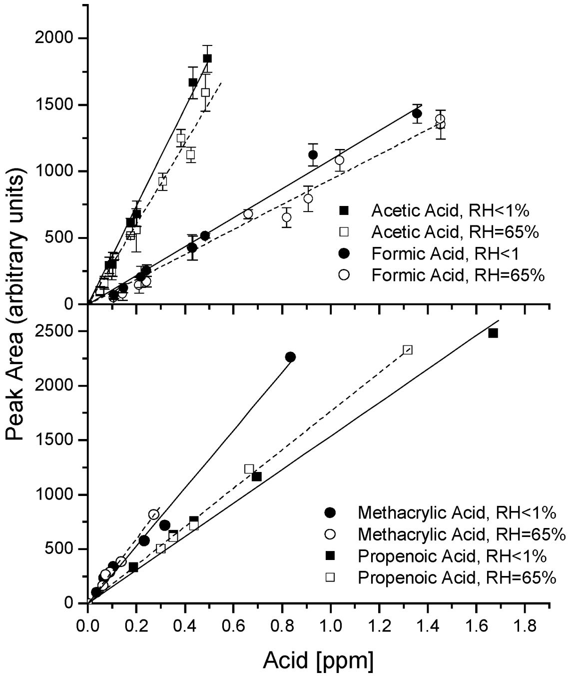


Figure 1. Calibration curves for SPME analysis of formic, acetic, methacrylic, and propenoic acids under dry and humid conditions.

Calibration curves for propenoic and methacrylic acids are also shown in Figure 1. Five concentrations of the acids were prepared (in random order) at each of two humidities. The resulting curves show good linearity from 50 to 1700 and from 50 to 800 ppb for propenoic and methacrylic acids, respectively, again with only slight humidity effects.

(5.2) Ozonolysis. A series of experiments investigating the production of organic acids from O_3 reactions with ethene, propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene were performed under dry (<1% RH) and humid (65 ± 5% RH) conditions. Initial experimental conditions, resulting acid yields, and related literature data are summarized in Tables 1 and 2. Data are plotted in Figures 2 and 4. In addition to acid yields, we measured primary carbonyl yields for propene, *trans*-2-butene, 2,3-dimethyl-2-butene, and isoprene; these results are shown in Table 3 and Figures 3 and 5. Overall uncertainties in the yields reported, including uncertainties from diffusion rates, fiber integrity, and SPME and GC/FID calibrations are as follows: formic, acetic, and 2-propenoic acids, ±20%; methacrylic acid, ±25%; and carbonyls, ±10%.

(5.2.1) Formic Acid. Formic acid was observed in high yield from the ozonolysis of each of the terminal alkenes, likely primarily as a result of decomposition of HMHP and HPMF on the SPME fiber or in the hot inlet of the GC/MS. Yields of formic acid under dry and humid conditions, respectively, were 36 ± 7 and 33 ± 6% for ethene, 28 ± 5 and 26 ± 5% for propene, and 52 ± 11% for isoprene, independent of RH. Yield curves were linear with $R^2 > 0.986$ for all cases.[30] From *trans*-2-butene, yields of up to 10% were observed, but with secondary behavior. The linearity of formic acid data from ethene, propene, and isoprene ozonolysis indicate its source is likely a combination of the direct pathway (R1) and decomposition of HPMF or HMHP, formed under dry or humid conditions, respectively. Our results are in good agreement with those of Wolff et al.,[63] who collected ethene ozonolysis samples in water-filled impingers and found formic acid yields of 36 ± 5 and 40 ± 13% under dry and humid conditions, respectively, supporting the notion that both HPMF and HMHP decompose heterogeneously to formic acid. Reports of direct formation of formic acid from

TABLE 1: Summary of Initial Conditions and Acid Yields for O_3 Reacting with Propene, *trans*-2-Butene, and 2,3-Dimethyl-2-butene

alkene	RH (%)	alkene concn (ppm)	cyclohexane concn (ppm)	acetic acid yield (%)	lit.
propene	<1	3.41	1680	2.7 ± 0.6	1[8]
	65	3.17	1530	1.8 ± 0.4	–
		2.85	1570		
trans-2-butene	<1	2.22		2.9 ± 0.6	0.8 ± 0.4;[26] 9.6 ± 12 [67]
		3.22	1700		
		3.16			
	65	3.41		2.3 ± 0.5	–
		5.39	1700		
		3.69			
2,3-dimethyl-2-butene	<1	3.03	2540	secondary; ~10	–
		3.57	2820		
	65	4.88	3880	secondary; ~8	–
		3.25	1720		

TABLE 2: Acid Products from the O_3 Reaction with Isoprene. Summary of Initial Conditions and Acid Yields

RH (%)	alkene (ppm)	scavenger (ppm)	acetic acid yield (%)	methacrylic acid yield (%)	propenoic acid yield (%)	lit.
<1	1.44	2670[a]	secondary; ~11%	5.5 ± 1	3.0 ± 1	methacrylic and propenoic: identified[29]
	1.93	2710[a]				
	2.59	1660[a]				
	1.46	420[b]				
65	1.61	3810[a]	secondary; ~12%	4.1 ± 1	1.5 ± 0.3	
	1.66	2790[a]				
	2.26	2550[a]				
	2.15	2290[c]				

[a] Cyclohexane. [b] Di-*n*-butyl ether. [c] 2-Butanol.

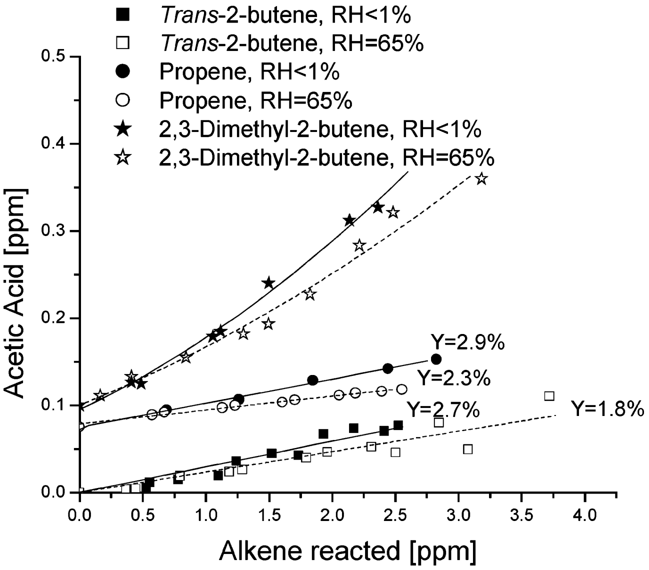


Figure 2. Formation of acetic acid under dry and humid conditions from 2,3-dimethyl-2-butene, propene, and *trans*-2-butene. The data for 2,3-dimethyl-2-butene and propene have been displaced vertically by 0.1 and 0.075 ppm, respectively.

ethene and propene indicate it is probably small; yields from several in situ studies using FTIR are 4–7%.[8,24]

The observed yield of formic acid from isoprene was 52 ± 11% under both dry and humid conditions, much higher than comparable measurements from the literature of formic acid, HMHP of HPMF, or SCI. The dry yield of direct formic acid has been reported as 3–6%,[24,25] while under humid conditions yields of HMHP range from 16 to 30%,[24,48] in line with SCI yields of about 27%.[48,64] It appears that the high amounts of formic acid measured in this study result partly from sources besides HPMF or HMHP, although it is not clear what those sources might be. The formic acid results are discussed in more detail by Orzechowska.[30]

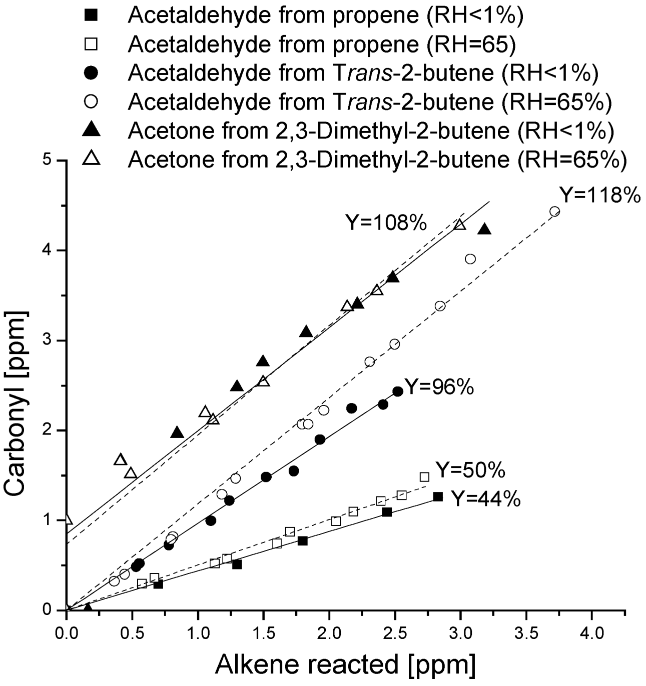


Figure 3. Carbonyl products: acetaldehyde from ozonolysis of propene and *trans*-2-butene; acetone from 2,3-dimethyl-2-butene. The acetone data have been displaced vertically by 1.0 ppm for clarity.

(5.2.2) Acetic, Propenoic, and Methacrylic Acids and Aldehydes. (5.2.2.1) Propene. Propene ozonolysis produced acetic acid with yields of 2.7 ± 0.6% at RH < 1%, and 1.8 ± 0.4% at RH = 65%, respectively (Table 1, Figure 2). This is substantially larger than the acetic acid yield reported by Herron and Huie[8] of 1%. Our acetaldehyde yields (Table 3, Figure 3) are 44 ± 4% at RH < 1% and 50 ± 5% at RH = 65% and are in good agreement with yields 45 ± 9 and 52 ± 3% reported by Tuazon et al.[65] and Grosjean and Grosjean,[66] respectively.

(5.2.2.2) *trans*-2-Butene. Yields of acetic acid from ozonolysis of *trans*-2-butene are 2.9 ± 0.6 and 2.3 ± 0.5% for dry and

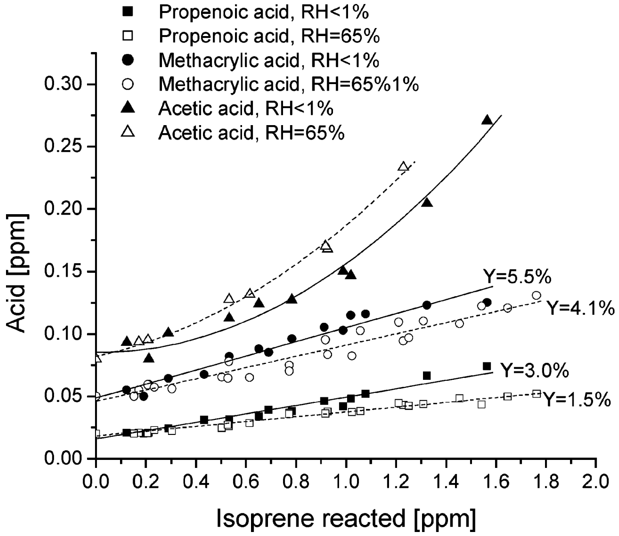
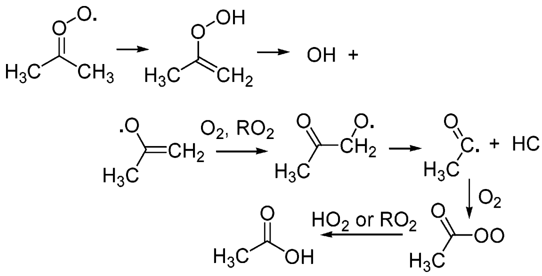


Figure 4. Acid formation from isoprene ozonolysis under dry and humid conditions. Data are vertically displaced for clarity: propenoic acid by 0.02 ppm, methacrylic acid by 0.05 ppm, and acetic acid by 0.08 ppm.

humid conditions, respectively. Acetic acid from *trans*-2-butene has been measured in two studies, with divergent results: Horie and Moortgat[26] reported a yield of 0.8 ± 0.4%, while Grosjean et al.[67] found 9.6%. Acetaldehyde formation was measured with yields of 96 ± 10 and 118 ± 12% under dry and humid conditions, respectively (Table 3 and Figure 3), in reasonable agreement with acetaldehyde yields of 109 ± 9 and 114 ± 14% reported by Tuazon et al.[65]

(5.2.2.3) 2,3-Dimethyl-2-butene. The yield curve for acetic acid produced by 2,3-dimethyl-2-butene ozonolysis indicates it has a "secondary" source, i.e., a formation pathway that includes a species that builds up over time, as indicated by a yield curve with an increasing slope. Yields are slightly higher at high RH (65%) than under dry conditions (Table 1, Figure 2) ~9 and 8% respectively. Acetic acid may be produced via the carbonyl oxide−OH generation channel:



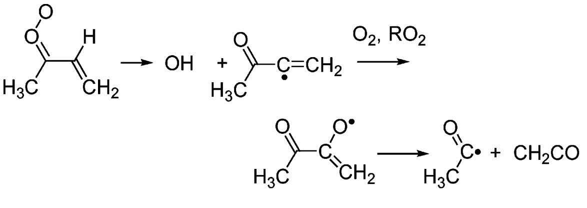
(R6)

Because of the steps involving HO_2 and/or RO_2 radicals, this pathway should exhibit secondary behavior. There are no reports in the literature on acetic acid production from 2,3-dimethyl-2-butene ozonolysis. The yield of acetone, the primary carbonyl product, was found to be independent of humidity at 108 ± 11% (Table 3, Figure 3). This value is in good agreement with several reports from the literature ranging from 101 to 114% (Table 3).

(5.2.2.4) Isoprene. Results for acetic, propenoic, and methacrylic acids are shown in Table 2 and Figure 4, and methacrolein and methyl vinyl ketone are shown in Table 3 and Figure 5.

Methacrylic acid is the only higher acid that can be formed directly from isoprene ozonolysis and is produced with yields of 5.5 ± 2 and 4.1 ± 1% under dry and humid conditions, respectively (Table 2). As far as we are aware no yields have been reported for methacrylic acid in the literature.

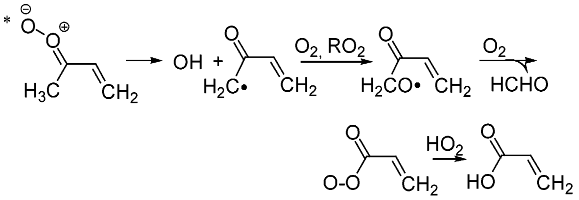
Acetic acid was generated with yields of 7 and 9% under dry and humid conditions, respectively (Figure 4), but the nonlinearity of the yield curve indicates a secondary source. There have been two reports of acetic acid from isoprene in the literature: Ruppert et al.[68] measured 5% under dry conditions and Chien et al.[29] observed but did not quantify this acid. There are several potential sources of acetic acid. Analogous to R6, acetic acid may arise from an OH generating carbonyl oxide decomposition, and also via an acylperoxy radical, is as follows:



(R7)

The coproduct of this pathway is ketene, which is not observed, although it is unclear if ketene would be observed with the flame ionization detector used in this study. Additional acetic acid may be formed from ozonolysis of methacrolein (via the analogue of R7). The methacrolein reaction may have a high yield of acetic acid, because the H-atom abstracted in the rearrangement is aldehydic and the leaving group is CO. Trace quantities also arise from ozonolysis of propene, which is a minor product of isoprene oxidation.[69]

We measured propenoic (acrylic) acid yields from isoprene ozonolysis of 3 ± 1 and 1.5 ± 0.3% (Table 2, Figure 4), under dry and humid conditions, respectively. Chien et al.[29] also detected propenoic acid as a pentafluorobenzyl derivative but did not quantify its yield. A mechanism that may produce propenoic acid begins with the same carbonyl oxide as for R7:



(R8)

Curiously, propenoic acid formation appears linear within the limits of the measurement under humid conditions, but slightly secondary under dry conditions (Figure 4).

Dry and humid yields of methacrolein were 33 ± 3 and 35 ± 4% and of methyl vinyl ketone were 10 ± 1; 14 ± 1% under dry and humid conditions, respectively (Table 3, Figure 5). Our values for both methacrolein and methyl vinyl ketone fall within the wide ranges of values reported in the literature (Table 3), although our methacrolein results show less humidity sensitivity than most other studies, and our methyl vinyl ketone yields are on the low end.

6. Discussion

SPME/GC/MS is a reliable and reasonably convenient method to quantify low molecular weight acids at concentrations from the mid-ppb range. The method has a few limitations: relatively high detection limits, the potential for heterogeneous reactions, and the requirement that absolute calibration standards be generated for each acid. SPME also offers an easy method to concentrate samples and introduce them to a GC via a standard liquid injection port and thus offers a convenient method for qualitative analyses.

TABLE 3: Carbonyl Product Yields

alkene	RH (%)	carbonyl	yield, this work (%)	lit. yield (%)
propene	<1	acetaldehyde	45 ± 5	45 ± 9,[65] 55 ± 3,[66] 45 [8]
	65		50 ± 5	
trans-2-butene	<1	acetaldehyde	96 ± 10	90 ± 8,[26] 109 ± 9 and 114 ± 14 [65]
	65		118 ± 12	117 ± 5 [51]
2,3-dimethyl-2-butene	<1	acetonerrr	108 ± 11	102 ± 13,[23] 101 ± 5,[66] 98 ± 9 and 114 ± 19 [65]
	65		108 ± 11	110 ± 5 [51]
isoprene	<1	methacrolein	33 ± 3	35,[25] 33,[64] 23 ± 2,[68] 35 ± 3,[48] 44,[66] and 38.7 ± 3 [70]
	65		35 ± 4	42 ± 4,[48] 29 ± 4,[68] 39 [25]
	<1	methyl vinyl ketone	9.7 ± 1	15,[25] 13,[64] 10 ± 1,[68] 17 ± 2,[48] 17 and 15.9 ± 1.3 [70]
	65		14 ± 1	24 ± 2,[48] 13 ± 2,[68] 20 [25]

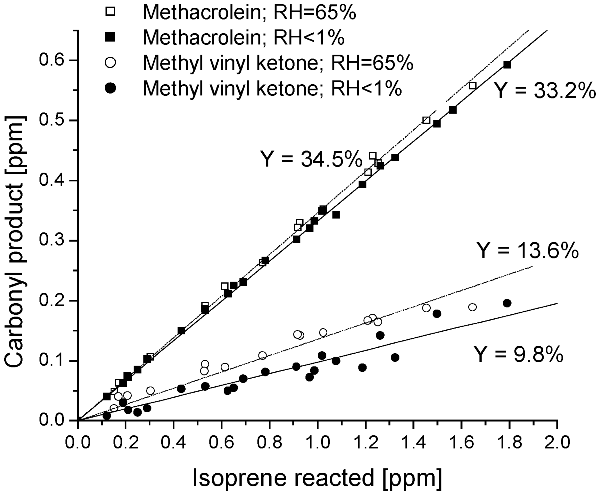


Figure 5. Carbonyl products from ozonolysis of isoprene.

Production of primary acids C_2 and larger from alkene ozonolysis is modest; from 2 to 5.5% for the compounds studied here. Yields of these acids drop off at higher humidity, by 20−33%. Primary acids from larger alkenes, the topic of the companion paper,[28] also exhibit reduced acid yields at high humidity. Clearly acids are not major products of SCI reactions with H_2O (R4c,d), although a very small amount of acid formation via this path cannot be ruled out.

Formation of smaller acids (C_{N-2}, C_{N-3}, and C_{N-4}) is a common feature of ozonolysis reactions (see also Orzechowska et al.[28]). Their formation is possible via multistep pathways involving HO_2 or RO_2 reactions with α-carbonyl (acyl) peroxy radicals generated by the decomposing *syn*-carbonyl oxides, which also generate OH. Yields vary from about 2% for hexanoic acid from 1-octene (see the companion paper in this issue[28]) and 1−3% for propenoic acid from isoprene to about 10% for acetic acid from isoprene and 2,3-dimethyl-2-butene, in this case exceeding the yields of acids with direct formation pathways. With the exception of acetic acid from isoprene, which has multiple sources, the yields of these acids appears to be correlated with the OH yields from the ozonolysis of the parent alkenes, consistent with the accepted mechanism for decomposing *syn*-carbonyl oxides. Other aspects of the behavior of these smaller acids are variable, however; for acetic and hexanoic acids, yields are nearly the same at dry and humid conditions, while propenoic acid production drops as humidity is increased. Further, while most of the acids have secondary yield curves, some are linear. All of these observations likely reflect complex behaviors of the RO_2 and HO_2 in the experiments. While dependent in unknown ways on NO_x, RO_2, and HO_2, formation of acetic acid from isoprene may be a significant global source of this common acid.

Quantifying aldehydes themselves is reasonably straightforward, yet there is a fair amount of variability in the literature (e.g., Table 3, and ref 70). The explanation of this scatter may lie in the α-hydroxyhydroperoxides that form in the SCI + H_2O reaction (R4a) which appear to decompose heterogeneously to aldehyde + H_2O_2.[51] Formation of α-hydroxyhydroperoxides varies depending on the experimental RH, and so does the opportunity for heterogeneous decomposition during analysis.

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