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Kinetics of the Gas-Phase Reactions of Alcohols, Aldehydes, Carboxylic Acids, and Water with the C13 Stabilized Criegee Intermediate Formed from Ozonolysis of 1-Tetradecene

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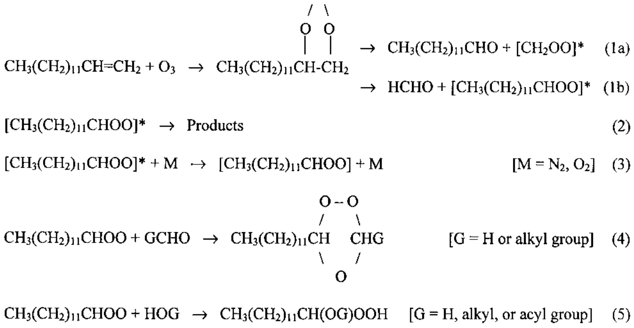
Previous studies in our laboratory have shown that the major aerosol products formed in gas-phase ozonolysis of 1-tetradecene in the presence of excess alcohols, carboxylic acids, water vapor, and aldehydes are α-alkoxytridecyl, α-acyloxytridecyl, α-hydroxytridecyl hydroperoxides, and secondary ozonides. These low volatility compounds are formed from reactions of C13 stabilized Criegee intermediates with the acidic compounds and aldehydes. To obtain a more quantitative understanding of the chemical mechanism and determine the importance of such reactions in the atmosphere, relative rate constant measurements were made using real-time quantitative thermal desorption particle beam mass spectrometry (TDPBMS) for aerosol analysis. The rates of reaction of methanol, 2-propanol, formic acid, water, and formaldehyde with C13 stabilized Criegee intermediates were measured relative to heptanoic acid. The results show that the reactivity of the studied compounds varies over 4 orders of magnitude and increases in the order: water $\ll$ methanol $<$ 2-propanol $\ll$ formaldehyde $<$ formic acid $<$ heptanoic acid. The rate constants depend primarily on the nature of the functional group and correlate well with the gas-phase acidities, indicating a relatively polar transition state for the reaction. The relative rate constants depend only slightly on the size of the reactant species and are similar to those measured previously for a C1 stabilized Criegee intermediate. The atmospheric implications of these results are also discussed.

Introduction

Alkenes compose a significant fraction of nonmethane hydrocarbons in urban areas, where the major sources include engine exhaust, gasoline and solvent vapors, and emissions from vegetation.[1,2] On the global scale, biogenic sources dominate hydrocarbon emissions, with the most abundant alkenes being isoprene and monoterpenes.[3] Gas-phase ozonolysis is an important tropospheric removal process for volatile alkenes,[4,5] which also produces OH radicals[6] and, for larger compounds, secondary organic aerosol (SOA). Details of the chemical mechanisms of SOA formation are not well understood, but the general process involves oxidative formation of low-volatility products followed by homogeneous nucleation or condensation onto preexisting particles. The resulting organic matter makes up a significant fraction of fine particles (diameter $< 2.5\ \mu$m), which play important roles in atmospheric phenomena such as cloud formation, light scattering, and heterogeneous chemistry, while also impacting human health.[7−9]

Laboratory studies of SOA formation from alkene oxidation have focused primarily on monoterpenes, which are $C_{10}H_{16}$ compounds generally thought to be the major contributors to global SOA.[10] The chemistry leading to SOA is very complex, however, and although a number of aerosol products from monoterpene reactions have been identified,[11] recent modeling studies indicate that the volatilities of these compounds are too high to explain the apparent role of organic species in atmospheric nucleation and particle growth.[12] Recently, we investigated SOA formation from the reaction of O_3 with 1-tetradecene (a surrogate for normal alkenes) in the presence of alcohols, carboxylic acids, aldehydes, and water.[13,14] Results obtained using a thermal desorption particle beam mass spectrometer (TDPBMS) for aerosol analysis showed that the major products are hydroperoxides, secondary ozonides, and peroxyhemiacetals, which have very low vapor pressures. The potential importance of peroxide compounds for aerosol formation in laboratory studies or the atmosphere has not been generally appreciated because they thermally decompose when analyzed by gas chromatography−mass spectrometry (the technique normally used for organic aerosol analysis). Although the contribution of normal alkenes to atmospheric aerosol formation is thought to be small,[15] the apparently simpler chemistry of normal, compared to cyclic, alkenes provides a good starting point for elucidating the chemical mechanisms of aerosol formation from alkene ozonolysis. Similar reactions might be important in the ozonolysis of branched and cyclic alkenes, and because the monoterpenes are relatively abundant and consist of acyclic and cyclic alkenes, their ozonolysis could lead to peroxide compounds of sufficiently high concentration and low volatility to contribute significantly to atmospheric nucleation and particle growth.

The products observed in our studies of 1-tetradecene ozonolysis can be explained by the generally accepted Criegee mechanism [4,16−19] shown below in reactions 1−5.



$$\mathrm{CH_3(CH_2)_{11}CH{=}CH_2 + O_3 \rightarrow CH_3(CH_2)_{11}\underset{\text{O-O-O}}{CH\text{-}CH_2} \rightarrow CH_3(CH_2)_{11}CHO + [CH_2OO]^*} \quad (1a)$$

$$\rightarrow \mathrm{HCHO + [CH_3(CH_2)_{11}CHOO]^*} \quad (1b)$$

$$\mathrm{[CH_3(CH_2)_{11}CHOO]^* \rightarrow Products} \quad (2)$$

$$\mathrm{[CH_3(CH_2)_{11}CHOO]^* + M \rightarrow [CH_3(CH_2)_{11}CHOO] + M} \quad [\mathrm{M = N_2, O_2}] \quad (3)$$

$$\mathrm{CH_3(CH_2)_{11}CHOO + GCHO \rightarrow CH_3(CH_2)_{11}CH\underset{O}{\overset{O-O}{\ }}CHG} \quad [\text{G = H or alkyl group}] \quad (4)$$

$$\mathrm{CH_3(CH_2)_{11}CHOO + HOG \rightarrow CH_3(CH_2)_{11}CH(OG)OOH} \quad [\text{G = H, alkyl, or acyl group}] \quad (5)$$

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Initially, ozone adds to the $>C{=}C<$ bond to yield an energy-rich primary ozonide, which decomposes to create a C1 excited Criegee intermediate $[CH_2OO]^*$ and tridecanal $[CH_3(CH_2)_{11}CHO]$ (reaction 1a), or a C13 excited Criegee intermediate $[CH_3(CH_2)_{11}CHOO]^*$ and formaldehyde [HCHO] (reaction 1b). The excited intermediates can undergo unimolecular reactions that lead to a variety of products, including OH radicals (and organic radical coproducts), aldehydes, carboxylic acids, and hydroxycarbonyls (reaction 2), or in air they can be stabilized through collisions with N_2 or O_2 (reaction 3). The stabilized Criegee intermediates (hereafter referred to as SCI) can react with other species, such as SO_2, CO, aldehydes, and acidic compounds. In the presence of aldehydes (GCHO, G = H or R, where R = alkyl group), the C13−SCI reacts to form a secondary ozonide (reaction 4). In the presence of acidic compounds (HOG), such as alcohols (G = R = alkyl group), carboxylic acids (G = C(O)R = acyl group), and water (G = H), C13−SCI reacts to form α-alkoxytridecyl, α-acyloxytridecyl, and α-hydroxytridecyl hydroperoxides (reaction 5). The hydroperoxides can subsequently react with aldehydes to form lower vapor pressure peroxyhemiacetals by the reaction

$$CH_3(CH_2)_{11}CH(OG_1)OOH + G_2CHO \rightarrow CH_3(CH_2)_{11}CH(OG_1)OOCH(OH)G_2 \quad (6)$$

which is known to occur in solution[20,21] and apparently takes place on the particle surface in our chamber experiments.[13]

In the present work, we describe a study of 1-tetradecene ozonolysis performed using a new technique that takes advantage of the real-time, quantitative capabilities of the TDPBMS and enables kinetic data for the reactions of the C13−SCI with various reactants to be obtained. The results provide a more quantitative understanding of the aerosol-forming pathways of the ozonolysis reaction mechanism. This information is necessary for determining the relevance of these reactions to the ambient atmosphere and for developing atmospheric models of alkene ozonolysis, which rely on results from laboratory studies.

Experimental Section

Relative-Rate Technique. Rate constants for reactions of C13−SCI with selected compounds (reactions 4 and 5), which are the major pathways to aerosol formation, were measured relative to a reference compound using the TDPBMS for quantitative analysis of the aerosol. For reactions of C13−SCI with a reference compound, HA (heptanoic acid), and a single competing reactant, CR, the bimolecular reactions are

$$\text{C13−SCI} + \text{HA} \xrightarrow{k_{\text{HA}}} \text{HPTH} \quad (7)$$

$$\text{C13−SCI} + \text{CR} \xrightarrow{k_{\text{HA}}} \text{product} \quad (8)$$

where k_{HA} and k_{CR} are the rate constants and HPTH is an abbreviation for α-hydroperoxytridecyl heptanoate $[CH_3(CH_2)_{11}CH(OC(O)(CH_2)_4CH_3)OOH]$, the product formed in the heptanoic acid reaction. It is straightforward to show that the ratio of the rate constants for these reactions is equal to

$$k_{\text{CR}}/k_{\text{HA}} = (([\text{HPTH}]_{\text{HA}}/[\text{HPTH}]_{\text{HA+CR}}) - 1)([\text{HA}]/[\text{CR}]) \quad (9)$$

where $[\text{HPTH}]_{\text{HA}}$ and $[\text{HPTH}]_{\text{HA+CR}}$ are the concentrations of HPTH formed in the absence and presence of a competing reactant, respectively, and [CR] and [HA] are the concentrations of competing reactant and heptanoic acid, respectively, which are present in large excess and hence constant during the reactions.

Environmental Chamber Reactions. Reactions of 1-tetradecene and O_3 were carried out at atmospheric pressure (~740 Torr) and room temperature (296 ± 3 K) in a 6800 L Teflon chamber filled with clean, dry air (<5 ppbv hydrocarbons, 0.1% RH). In all reactions, 0.13−0.64 ppmv 1-tetradecene $[CH_3(CH_2)_{11}CH{=}CH_2]$, 2.1−3.3 ppmv ozone, and 0.5−2.5 ppmv heptanoic acid $[CH_3(CH_2)_5C(O)OH]$ were added to the chamber. The concentrations of competing reactants were 2.5 ppmv formic acid [HC(O)OH], 12.5 ppmv formaldehyde [HCHO], 1740 ppmv methanol $[CH_3OH]$ and 2-propanol $[(CH_3)_2CHOH]$, and 12 400 ppmv water vapor, with only one of these being present in a given experiment. Because unimolecular decomposition of the stabilized Criegee intermediate could potentially compete with bimolecular reactions,[22] in one experiment, we also measured the amount of HPTH formed with 7.5 ppmv (instead of 2.5 ppmv) of added heptanoic acid in the absence of a competing reactant. There was no significant difference, indicating that unimolecular decomposition of C13−SCI is negligible in our experiments. Approximately 1000 ppmv of cyclohexane [cyclo-C_6H_{12}] was also added in all reactions, except for those with methanol and 2-propanol. The concentrations of cyclohexane, methanol, and 2-propanol were sufficient to scavenge >95% of the OH radicals formed in the alkene-O_3 reaction,[23] thereby eliminating secondary reactions between 1-tetradecene and OH. For an OH yield ~0.2,[6] the concentration of products (e.g., aldehydes and ketones) from the scavenger + OH reactions is ~0.13 ppmv in all reactions except for the one with formaldehyde, for which the concentration would be ~0.025 ppmv. These species can subsequently react with C13−SCI, but even if the rate constants are similar to heptanoic acid, which is the most reactive species studied, their concentrations are too low for them to compete significantly with the added reactants. For the formaldehyde reaction, the concentration of 1-tetradecene was reduced from 0.64 ppmv to 0.13 ppmv in order to minimize reaction of C13−SCI with formic acid formed by reaction of formaldehyde with C1−SCI. Assuming that 50% of the 1-tetradecene reaction leads to excited C1 Criegee intermediates[4,24] and that 50% of these are stabilized and then react solely with formaldehyde to produce 44% formic acid,[19] the concentration of formic acid will be ~0.014 ppmv. Even if the rate constant for the formic acid reaction is 20× greater than the value for formaldehyde,[19] the effect of formic acid on the measurements is negligible for the 12.5 ppmv concentration of formaldehyde used here.

Measured quantities of reactants were added to the chamber as gases in a clean air stream. During additions a fan was run to ensure mixing, but was turned off a few minutes after the reaction was initiated by adding O_3. A known pressure and volume of formaldehyde was obtained by evaporating paraformaldehyde into an evacuated glass bulb. Ozone was added as ~2% O_3/O_2 from a Welsbach T-408 ozone generator, and then the O_3 concentration in the chamber was measured with a Dasibi 1003-AH O_3 analyzer. The other organics and water were vaporized into the air stream by heating. Low-volatility tetracosane $[C_{24}H_{50}]$ or dioctyl sebacate $[(CH_2)_4CO_2CH_2CH(C_2H_5)(CH_2)_3CH_3]_2$ was used to generate seed particles, which formed by homogeneous nucleation of the hot vapor as it cooled. The peak in the seed particle size distribution was $< 0.1\ \mu$m diameter and typical chamber concentrations were $\sim 4 \times 10^4$ particles cm^{-3}. These particles served as nuclei for condensation of reaction products and maintained the SOA size distribution in the ~0.1−0.3 μm size range, with a mass mean diameter of ~0.2−0.3 μm. Particles of this size are sampled into the TDPBMS with near-unit efficiency. Aerosol size distributions were measured using a scanning electrical mobility spectrometer,[25,26] and chamber particles were sampled directly into the TDPBMS without size selection.

TDPBMS Calibration and Analysis of Chamber Aerosol. A detailed description of the TDPBMS and the procedures and equations used for real-time quantitative particle analysis are given elsewhere.[25] Briefly, calibration or chamber particles are sampled into the TDPBMS through a 100 μm orifice at 0.075 L min^{-1}, which reduces the pressure from atmospheric to ~2 Torr. The particles enter a series of aerodynamic lenses used for particle focusing and form a very narrow, low divergence particle beam.[27,28] The particles then pass through two flat-plate skimmers, which separate three differentially pumped chambers, and enter a high-vacuum chamber at ~5 × 10^{-8} Torr. The chambers are evacuated using turbomolecular pumps and backed by an oil-free mechanical scroll pump. In the high-vacuum chamber, particles impact with nearly 100% efficiency on a V-shaped molybdenum foil vaporizer that is situated outside the mass spectrometer ionizer and is resistively heated to ~165 °C. The particles are continuously vaporized and a portion of the desorbing molecules diffuse into an ABB Extrel MEXM 500 quadrupole mass spectrometer. The vapor is ionized by 70 eV electrons, and the mass-filtered ions are detected using a conversion dynode/pulse counting detector. During analysis, the mass spectrometer is scanned from m/z 10−250 in ~50 s.

For these experiments, an HPTH calibration standard was prepared by bubbling 2% O_3/O_2 at 1.5 L min^{-1} for 3 min through a solution containing 1 mL of 1-tetradecene and 3 mL of heptanoic acid in 40 mL of cyclohexane. The reacted solution was then diluted to 250 mL with cyclohexane and atomized in a Collison atomizer using clean air. The resulting mist was sent through an activated charcoal diffusion drier to evaporate the cyclohexane, unreacted 1-tetradecene, volatile products, and heptanoic acid, leaving submicron aerosol particles comprising only HPTH. The aerosol then flowed through a bipolar charger, which produces mostly neutral and singly charged particles, and through a differential mobility analyzer (DMA),[29,30] which separates charged particles according to their electrical mobility and provides a near-monodisperse aerosol for calibration. The particle current at the exit of the DMA was measured using a Faraday cage and electrometer and a known fraction of the flow was sampled into the TDPBMS. The diameter of particles used for calibrations was ~0.23 μm, a size which approximately matches the peak in the chamber aerosol mass distribution, and therefore yields similar mass-averaged TDPBMS sampling efficiencies for chamber and calibration particles.

The concentration of HPTH in chamber particles was calculated from the equation

$$C_{\mathrm{sample}} = [S_{\mathrm{sample}}/S_{\mathrm{cal}}][E_{\mathrm{cal}}/E_{\mathrm{sample}}][\gamma\pi\rho_{\mathrm{p}}D_1{}^3\mathrm{I}_{\mathrm{DMA}}/6V_{\mathrm{DMA}}e]_{\mathrm{cal}} \tag{10}$$

where $S_{\mathrm{sample}}/S_{\mathrm{cal}}$ and $E_{\mathrm{cal}}/E_{\mathrm{sample}}$ are the ratios of the mass spectral signals and transport efficiencies of sample and calibration particles, respectively, and the last term in brackets contains quantities related to the calibration particles. The quantity γ is a correction factor for the small fraction of multiply charged particles that exit the DMA, ρ_{p} is the particle density, D_1 is the diameter of the singly charged particles, I_{DMA} is the electrometer current measured for particles exiting the DMA, V_{DMA} and V_{TDPBMS} are the volumetric flow rates of air exiting the DMA and entering the TDPBMS, and e is the electron charge. The ratio $E_{\mathrm{cal}}/E_{\mathrm{sample}}$ is assumed to be unity since the composition and mass mean diameter of the chamber and calibration particles are similar and transport efficiencies normally have only a slight dependence on particle size in the 0.1−0.3 μm size range. The HPTH density was assumed to be 0.85 g cm^{-3}, which is typical for high molecular weight organics. The remaining quantities were all measured, but only $S_{\mathrm{sample}}/S_{\mathrm{cal}}$ varies between experiments.

Chemicals. The fine chemicals dioctyl sebacate (DOS, 90%), formic acid (96%), heptanoic acid (99%), tetracosane (99%), and 1-tetradecene (tech, 92%) were obtained from Aldrich Chemical Co., Inc. HPLC grade cyclohexane, Karl Fischer grade methanol, and Optima grade 2-propanol were obtained from Fisher Scientific.

Results and Discussion

In a complex reaction mechanism such as the one shown above, the importance of any particular reaction channel depends on the relative rates of competing reactions. For 1-tetradecene, the pathways of interest for aerosol formation include the split between the C1 and C13 excited intermediates (reactions 1a and 1b), the split between excited intermediate reactions and stabilization (reactions 2 and 3), and the competing reactions between stabilized intermediates and alcohols, carboxylic acids, aldehydes, water, CO, SO_2, and so forth (reactions 4 and 5). Studies on terminal alkenes as large as 1-decene consistently show that reactions 1a and 1b occur in a 1:1 ratio,[4,24] so we have not attempted to quantify these pathways. The relative rate constants for reaction of formic acid, formaldehyde, water, CO, and SO_2 with the C1 stabilized intermediate formed from ozonolysis of ethene have been measured,[4,17,19,31−33] and relative to water range from ~14 000:1 for formic acid to ~20:1 for CO. Here, we measured the relative rate constants for reactions of the much larger C13−SCI with water and a wider variety of organic species, including methanol, 2-propanol, formic acid, heptanoic acid, and formaldehyde. Reactions with CO and SO_2 were not studied but are expected to be much slower than with water under ambient and typical laboratory conditions. We also quantified the fraction of C13−SCI formed because few data are available for terminal alkenes.[4,6]

The relative rate method we used for these measurements requires that the reference compound being quantified be of sufficiently low vapor pressure that it partitions entirely into the particle phase. Furthermore, evaporation of aerosol during TDPBMS sampling and calibration, and from variations in the chamber temperature, should be negligible. For these reasons, we chose heptanoic acid as the reference compound because the HPTH produced by reaction with C13−SCI has an estimated vapor pressure of ~10^{-11} Torr,[13] and is therefore entirely in the particle phase. In addition, HPTH calibration aerosol could be easily prepared by employing the liquid-phase version of the ozonolysis reaction.[13,34] The TDPBMS mass spectra of HPTH calibration and chamber particles are shown in Figure 1. The signal at m/z 113 was used to quantify HPTH in the chamber reactions because this is the largest peak in the HPTH mass spectrum, but a very small peak in all the aerosol compounds formed in competing reactions.[13,14]

A fraction of the m/z 113 peak is contributed by the peroxyhemiacetal formed by reaction of HPTH with tridecanal (reaction 6). However, we have shown previously[13] by using a temperature-programmed TDPBMS technique[35] to separate the two compounds according to volatility that the fraction is only ~15%. Because the mass spectrum of HPTH and the peroxyhemiacetal are nearly identical,[13] this reaction should have little

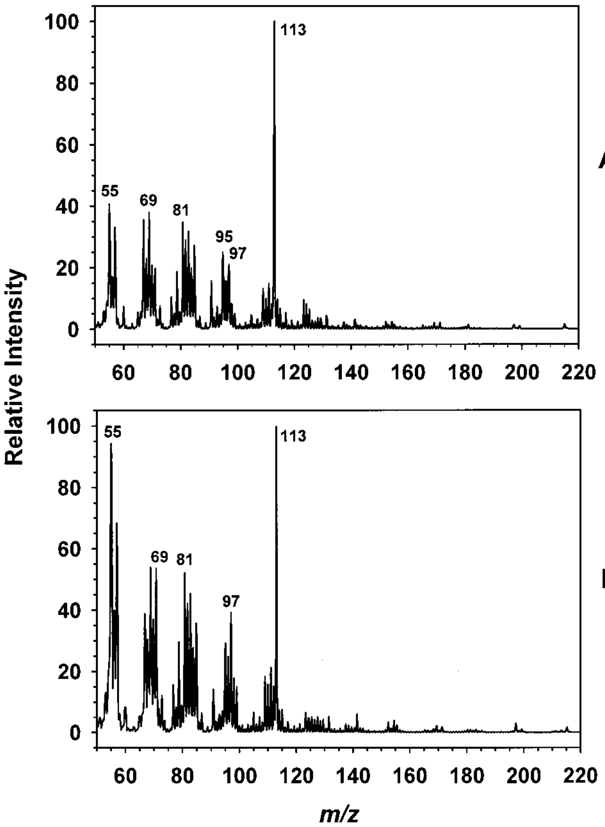


Figure 1. Real-time TDPBMS mass spectra of HPTH (α-hydroperoxytridecyl heptanoate) in (A) calibration and (B) chamber particles, formed by ozonolysis of 1-tetradecene in excess heptanoic acid in solution and the chamber, respectively. The signal at *m/z* 113 was used to quantify HPTH in the chamber reactions.

effect on the results. Although this may appear to be a somewhat convoluted way to measure gas-phase processes, because of the difficulty in obtaining standards for quantification and the labile nature of the peroxide products, analysis by more traditional methods would probably be very difficult.

Figure 2a depicts real-time measurements of HPTH formed during ozonolysis of 1-tetradecene in the presence of heptanoic acid, a 1:700 molar ratio of heptanoic acid:methanol, and a 1:700 molar ratio of heptanoic acid:2-propanol. The HPTH concentration decreases measurably when alcohols are present because of the competing reactions with C13−SCI. Similar behavior is observed in the other reactions. Relative rate constants were calculated using eq 9, the constant values of [HA] and [CR] calculated from the amounts added, and measurements of $[\mathrm{HPTH}]_{\mathrm{HA}}$ and $[\mathrm{HPTH}]_{\mathrm{HA+CR}}$ made 60−70 min after the start of reaction. At this point, the reaction is almost complete, and HPTH concentrations reach a plateau that is maintained by the balance between the slow rates of aerosol formation and particle loss to the walls. Figure 2b shows the decay in HPTH signal 3−4 h after the start of the reaction in the presence of heptanoic acid, which indicates an average wall loss rate of HPTH aerosol of ~15% hr^{-1}. From replicate measurements of HPTH formed in the presence of heptanoic acid with and without the competing reactant, formic acid, the precision of the relative rate constant measurements is estimated to be ~35%. The accuracy of TDPBMS measurements of C_{sample} has previously been estimated to be ~20% by using eq 10 and the uncertainty in each quantity in the equation.[25] Because eq 9 involves the ratio of two such measurements, the corresponding uncertainty in the accuracy of the relative rate constants is ~30%.

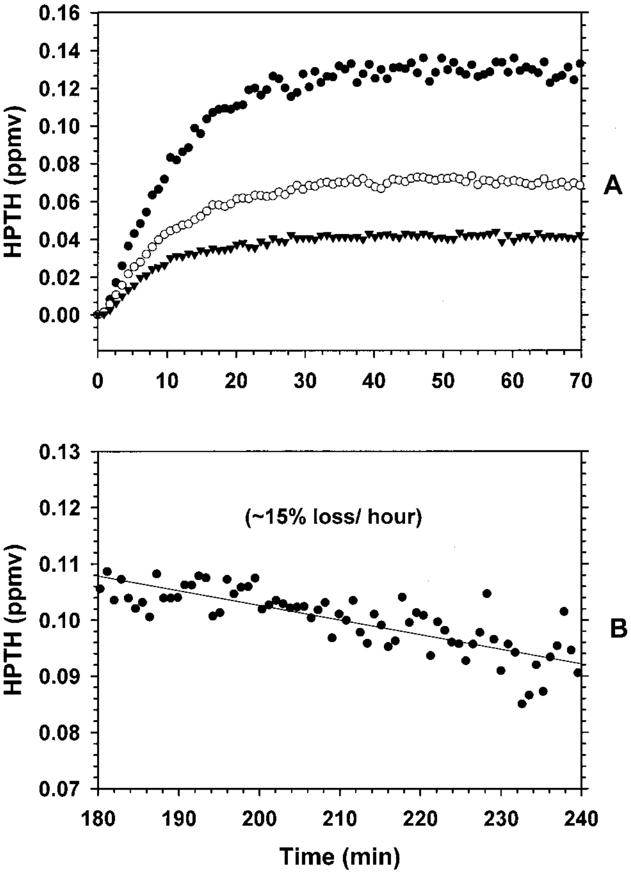


Figure 2. Real-time measurement of HPTH (α-hydroperoxytridecyl heptanoate) formed (A) during the first 70 min of ozonolysis of 1-tetradecene in the presence of excess (solid circles) heptanoic acid, (open circles) 1:700 molar ratio of heptanoic acid and methanol, and (solid triangles) 1:700 molar ratio of heptanoic acid and 2-propanol, and (B) during the 180−240 min period in the heptanoic acid reaction. The decay of signal in B corresponds to a particle wall loss rate of ~15% hr^{-1}.

The rate constant, k_{O3}, for the pseudo first-order reaction of 1-tetradecene with O_3, can be estimated by fitting the data in Figure 2A for reaction in the presence of heptanoic acid without a competing reactant to the equation

$$-\ln(1-([\mathrm{HPTH}]/(\alpha[1-\mathrm{tetradecene}]_0))) = k_{\mathrm{O3}}[\mathrm{O_3}]t \quad (11)$$

which can be derived from the rate and mass balance equations

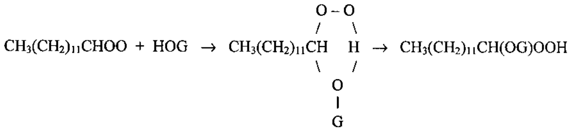
$$\ln([1-\mathrm{tetradecene}]/[1-\mathrm{tetradecene}]_0) = -k_{\mathrm{O3}}[\mathrm{O_3}]t \quad (12)$$

$$[1-\mathrm{tetradecene}] = [1-\mathrm{tetradecene}]_0 - ([\mathrm{HPTH}]/\alpha) \quad (13)$$

where [HPTH] is the time-dependent HPTH concentration, α is the fraction of reacted 1-tetradecene that forms C13−SCI, $[\text{1-tetradecene}]_0$ is the initial concentration of 1-tetradecene, $[O_3]$ is the approximately constant value of O_3, and t is time. The calculated rate constant is quite sensitive to the value of α. An upper limit to α can be estimated using the data shown in Figure 2A and 2B for the heptanoic acid reaction without a competing reactant. Assuming that all of the initial 0.64 ppmv of 1-tetradecene reacts in 60−70 min, and that the amount of HPTH formed in this time, when corrected for a 15% loss to the walls, is 0.15 ppmv, gives a yield of C13−SCI of 0.23. The kinetic plot obtained using this value of α is shown is Figure 3, and from the slope of the line = 0.0013, $[O_3]$ = 2.4 ppmv, and eq 11, we obtain $k_{\mathrm{O3}} = 2.2 \times 10^{-17}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. This calculation does not correct for wall losses, but these should only be ~6% for the time period considered. The rate constant is somewhat larger than those measured for terminal alkenes from propene through 1-decene, which are in the range 0.9–1.4 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1} at room temperature, although with the exception of 1-decene the values tend to increase with increasing carbon number.[4] Extrapolation of the rate constants for these compounds (neglecting 1-decene) to 1-tetradecene gives a value of ~1.8 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1}. If we instead use a rate constant of 1.1 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1}, which is an average of the literature values for terminal alkenes, and a value of $[O_3] = 2.4$ ppmv, we estimate that after 60–70 min the reaction is ~90% complete. For this case, the value of α is then 0.26. These stabilized Criegee intermediate yields are slightly larger than the value of 0.22 reported for 1-octene,[36] but this is expected since beyond ethene the yield tends to increase (apparently to ~0.28 for zero OH yield, according to Paulson et al.[6]) as the size of the Criegee intermediate increases.

The experimental conditions and rate constant ratios for the reactions of C13–SCI with methanol, 2-propanol, formic acid, formaldehyde, and water, measured relative to heptanoic acid, are given in Table 1. The reactivity spans 4 orders of magnitude and increases in the order: $H_2O \ll CH_3OH < (CH_3)_2CHOH \ll HCHO < CH(O)OH < CH_3(CH_2)_5C(O)OH$. The general trend is water ≪ alcohols ≪ aldehydes < carboxylic acids, with rates within a particular compound class tending to increase with molecular size. When expressed relative to reaction with water, the rate constants are 1:22:50:2700:6700:17000 for H_2O:CH_3OH:$(CH_3)_2CHOH$:HCHO:HC(O)OH:$CH_3(CH_2)_5C(O)OH$, as shown in Table 2. Also listed are literature values[19,32] of the relative rate constants for reactions of formic acid[19] and formaldehyde[19,32] with the CH_2OO SCI formed in the gas-phase ozonolysis of ethene. The values generally agree with those measured for C13–SCI to within a factor of ~2–3, with the CH_2OO rate constants being larger for formic acid and smaller for formaldehyde.

All of the compounds investigated, except for formaldehyde, react according to reaction 5 to form hydroperoxides. The transition state for this reaction is probably a five-membered ring similar to that of the secondary ozonide formed by formaldehyde (reaction 4), except that an H atom replaces a C atom in the ring.



$$CH_3(CH_2)_{11}CHOO + HOG \rightarrow CH_3(CH_2)_{11}\overset{O-O}{\underset{\underset{G}{|}}{\underset{O}{CH\quad H}}} \rightarrow CH_3(CH_2)_{11}CH(OG)OOH \qquad (14)$$

Because reaction 14 involves breaking the O–H bond in the compound that reacts with C13–SCI, one would expect that the height of the energy barrier leading to reaction would depend on the strength of the O–H bond: the weaker the bond the faster the reaction. In Table 2, we list the bond dissociation energies, BDE, for breaking the acidic reactant, HX, into two neutral products[37]

$$HX \rightarrow H + X \qquad (15)$$

and the free energy change, $\Delta G_{acidity}$, for the gas-phase dissociation of HX into ions

$$HX \rightarrow H^+ + X^- \qquad (16)$$

The rate constants do not correlate with BDE, but do correlate well with $\Delta G_{acidity}$, such that as $\Delta G_{acidity}$ decreases and dissociation into ions becomes more energetically favorable, the rate constant increases. The same trend would be seen using values of $\Delta H_{acidity}$, which are all ~30 kJ mol^{-1} less than $\Delta G_{acidity}$. This correlation suggests that the reaction involves a relatively polar transition state, which is consistent with computations[38] indicating that Criegee intermediates have a zwitterionic structure that becomes increasingly ionic as the O–O bond is elongated, as would occur during reaction 14. A plot of $\ln(k_{CR}/k_{H2O})$ vs $\Delta G_{acidity}$, which is generally referred to as a Hammett plot, is shown in Figure 4. The relationship is linear, as has been observed for various types of organic reactions in solution.[39] Because of the similarity in the relative rates of reactions of these species with stabilized $CH_3(CH_2)_{11}$-CHOO and CH_2OO intermediates, this relationship can probably be used to estimate relative rate constants for reactions of unsubstituted intermediates with acidic compounds for which $\Delta G_{acidity}$ is known.

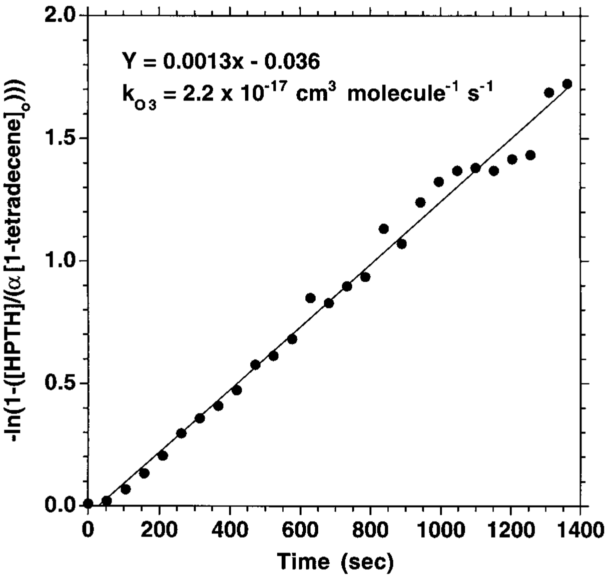


Figure 3. Kinetic plot for the chamber reaction of 1-tetradecene + O_3 in the presence of excess heptanoic acid, leading to formation of HPTH (α-hydroperoxytridecyl heptanoate).

It appears, therefore, that the relative rates at which organic species react with SCI depend strongly on the nature of the functional group(s) on the reactant molecule, especially their acidic properties, but only weakly on the size of the reactant molecule or the SCI. This does not mean that all SCI react at the same absolute rate with a particular reactant, only that the relative reactivities for species such as those studied here appear to be similar for SCI of different sizes.

Implications for Atmospheric Chemistry. The importance of particular reactions of SCI with competing compounds under ambient or laboratory conditions depends on the relative reaction rate constants and compound concentrations. The relative rates of reaction of alcohols, aldehydes, carboxylic acids, and water with C13–SCI formed in the 1-tetradecene ozonolysis reaction have been measured here using quantitative TDPBMS. The concentrations of competing reactants in the atmosphere can be estimated from the literature. Sources of carboxylic acids include direct emissions from anthropogenic sources such as biomass combustion and automobile exhaust and also photochemical production from various precursors, as in alkene ozonolysis. Ambient concentrations are highest for formic and acetic acid and are usually in the range of ~1–10 ppbv, with the higher concentrations in urban areas.[40,41] Automobile exhaust is also a significant source for formaldehyde and acetaldehyde,

TABLE 1: Relative Rate Constants for $CH_3(CH_2)_{11}CHOO$ Reactions with Organic Compounds and Water[a]

competing reactant	[1-tetradecene] (ppmv)	[HA] (ppmv)	[CR] (ppmv)	$[HPTH]_{HA}$/ $[HPTH]_{HA+CR}$	[CR]/ [HA]	k_{CR}/ k_{HA}
heptanoic acid	0.64	2.5				1.0
formic acid	0.64	2.5	2.5	1.4	1	0.40
formaldehyde	0.13	0.5	12.5	5.0	25	0.16
2-propanol	0.64	2.5	1740	3.1	700	0.0030
methanol	0.64	2.5	1740	1.9	700	0.0013
water	0.64	1.2	12 400	1.6	10 000	0.000 060

[a] Notation: HA = heptanoic acid; CR = competing reactant; HPTH = α-hydroperoxytridecyl heptanoate product from reaction of $CH_3(CH_2)_{11}CHOO$ with heptanoic acid

TABLE 2: Relative Rate Constants for $CH_3(CH_2)_{11}CHOO$ and CH_2OO Reactions, Thermochemistry, and Implications for Atmospheric Chemistry[a]

competing reactant	k_{CR}/k_{H2O} (for $CH_3(CH_2)_{11}CHOO$ this study)	k_{CR}/k_{H2O} (for CH_2OO literature)	$\Delta G_{acidity}$ (kJ mol^{-1})	BDE (kJ mol^{-1})	[CP]/[HTHP] (for $CH_3(CH_2)_{11}CHOO$ ambient)[b]	[CP]/[HTHP] (for $CH_3(CH_2)_{11}CHOO$ laboratory)[c]
heptanoic acid	17 000		1418	444	0.03	3
formic acid	6700	14 000[19]	1415	444	0.01	1
formaldehyde	2700	1100,[32] 700[19]			0.005	0.5
2-propanol	50		1541	438	0.000 08	0.008
methanol	22		1563	437	0.000 03	0.003
water	1.0		1607	499	1.0	1.0

[a] Notation: CR = competing reactant; CP = hydroperoxide product from reaction of $CH_3(CH_2)_{11}CHOO$ with competing reactant; HTHP = α-hydroxytridecyl hydroperoxide product from reaction of $CH_3(CH_2)_{11}CHOO$ with water [b] Ratio of products formed by reaction of 10 ppbv competing reactant and 6 × 10^6 ppbv water (20% RH) [c] Ratio of products formed by reaction of 1 ppmv competing reactant and 6 × 10^3 ppmv water (20% RH)

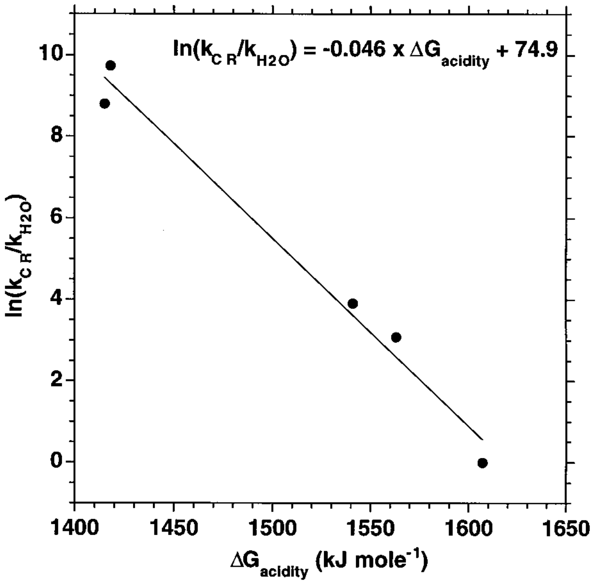


Figure 4. Hammett plot of relative rate constant vs reactant acidity, $\Delta G_{acidity}$, for the reactions of C13−SCI with water and acidic organic compounds.

the most abundant aldehydes. Ambient concentrations of formaldehyde are usually ~1−10 ppbv and can reach levels up to ~100 ppbv in some cities, whereas acetaldehyde is slightly lower.[41,42] Major sources of alcohols are direct emissions, including from fuels containing alcohol additives and biogenic emitters such as terrestrial plants.[42] Methanol, the most abundant alcohol in the lower troposphere, is usually found at concentrations of ~1−40 ppbv.[42] Ethanol concentrations as high as ~70 ppbv have been measured in areas where it is used in fuel.[43] Concentrations of water vapor depend on relative humidity and temperature, but are ~3 × 10^3 − 3 × 10^4 ppmv at 298 K and 10−100% RH. In laboratory studies of alkene chemistry, it is common to use alkene concentrations in the ppmv range, which can result in aldehyde and carboxylic acid concentrations of the same order of magnitude. In Table 2, the amounts of competing products, CP, formed relative to α-hydroxytridecyl hydroperoxide from the H_2O reaction, HTHP, are calculated for 20% relative humidity and organic reactant concentrations of 10 ppbv (the high end of the ambient concentration range) and 1 ppmv. This provides an upper estimate to the potential contribution of these reactions to ambient and laboratory reactions.

Although water reacts with SCI much more slowly than organics, especially carboxylic acids, the much higher ambient concentration of water vapor is calculated to result in the formation of primarily α-hydroxyalkyl hydroperoxides, with ~2−3 orders of magnitude lower concentrations of α-acyloxyalkyl hydroperoxides and secondary ozonides from the reactions of SCI with heptanoic acid, formic acid and formaldehyde, and negligible amounts of α-alkoxyalkyl hydroperoxides from reactions with methanol and 2-propanol. Hydroperoxides (including those formed in low-NO_x environments by OH and NO_3 oxidation of hydrocarbons)[4] can subsequently react with aldehydes to form relatively stable, low-volatility peroxyhemiacetals (reaction 6). The SCI reaction pathways, including those with water vapor, therefore provide a means by which alkenes can be converted into low-volatility compounds that are much more likely than the parent compounds to accumulate in particulate matter. Even if formed in low concentrations, these products could play an important role in atmospheric nucleation and particle growth, providing they have vapor pressures less than ~10^{-10} Torr.[12] Under typical laboratory conditions, the impact of reactions with organic compounds is more pronounced, because of the much higher concentrations of carboxylic acids and aldehydes present when initial alkene concentrations are in the ppmv range. In this case, the chemistry will be far different from that observed in the ambient atmosphere, meaning that caution may be required when extrapolating the results of laboratory experiments to the atmosphere. Although we have been dealing here with normal alkenes, the measured relative rate constants and the conclusions may also apply to cyclic alkenes that have one or no substituents on the doubly bonded carbons. Upon reaction with O_3 the rings in these compounds open to form linear Criegee intermediates similar to those of normal alkenes, except with a carbonyl group on one end.[4] These species may react similarly with acidic compounds and aldehydes. They may also react intramolecularly to form secondary ozonides, especially in the ambient atmosphere where intermolecular reactions are slower, reducing the SCI yields. The reactivity of substituted SCI and the stabilities of the various products warrants further study.

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