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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · FEBRUARY 2012

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Studies of the Gas Phase Reactions of Linalool, 6-Methyl-5-hepten-2-ol and 3-Methyl-1-penten-3-ol with O_3 and OH Radicals

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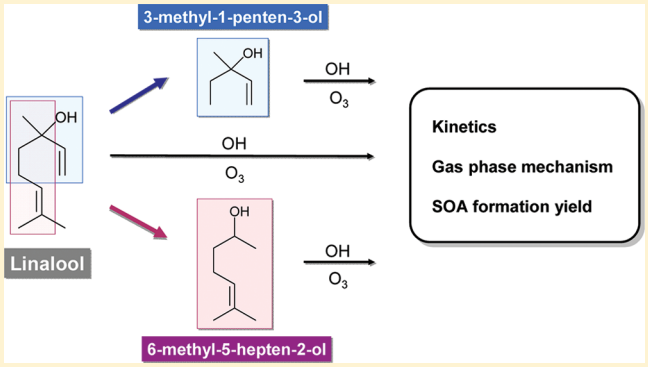
Supporting Information

ABSTRACT: The reactions of three unsaturated alcohols (linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol) with ozone and OH radicals have been studied using simulation chambers at $T \sim 296$ K and $P \sim 760$ Torr. The rate coefficient values (in cm^3 $molecule^{-1}$ s^{-1}) determined for the three compounds are linalool, $k_{O3} = (4.1 \pm 1.0) \times 10^{-16}$ and $k_{OH} = (1.7 \pm 0.3) \times 10^{-10}$; 6-methyl-5-hepten-2-ol, $k_{O3} = (3.8 \pm 1.2) \times 10^{-16}$ and $k_{OH} = (1.0 \pm 0.3) \times 10^{-10}$; and 3-methyl-1-penten-3-ol, $k_{O3} = (5.2 \pm 0.6) \times 10^{-18}$ and $k_{OH} = (6.2 \pm 1.8) \times 10^{-11}$. From the kinetic data it is estimated that, for the reaction of O_3 with linalool, attack at the R−CH═C$(CH_3)_2$ group represents around (93 ± 52)% ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{linalool}$) of the overall reaction, with reaction at the R−CH═CH_2 group accounting for about (1.3 ± 0.5)% ($k_{3\text{-methyl-1-penten-3-ol}}/k_{linalool}$). In a similar manner it has been calculated that for the reaction of OH radicals with linalool, attack of the OH radical at the R−CH═C$(CH_3)_2$ group represents around (59 ± 18)% ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{linalool}$) of the total reaction, while addition of OH to the R−CH═CH_2 group is estimated to be around (36 ± 6)% ($k_{3\text{-methyl-1-penten-3-ol}}/k_{linalool}$). Analysis of the products from the reaction of O_3 with linalool confirmed that addition to the R−CH═C$(CH_3)_2$ group is the predominant reaction pathway. The presence of formaldehyde and hydroxyacetone in the reaction products together with compelling evidence for the generation of OH radicals in the system indicates that the hydroperoxide channel is important in the loss of the biradical $[(CH_3)_2COO]^*$ formed in the reaction of O_3 with linalool. Studies on the reactions of O_3 with the unsaturated alcohols showed that the yields of secondary organic aerosols (SOAs) are higher in the absence of OH scavengers compared to the yields in their presence. However, even under low-NO_X concentrations, the reactions of OH radicals with 3-methyl-1-penten-3-ol and 6-methyl-5-hepten-2-ol will make only a minor contribution to SOA formation under atmospheric conditions. Relatively high yields of SOAs were observed in the reactions of OH with linalool, although the initial concentrations of reactants were quite high. The importance of linalool in the formation of SOAs in the atmosphere requires further investigation. The impact following releases of these unsaturated alcohols into the atmosphere are discussed.



1. INTRODUCTION

Unsaturated alcohols have been the subject of many studies in the last two decades due to their emissions in large amounts from biogenic and anthropogenic sources and their important role in atmospheric chemistry. This is the case for methyl-butenols (e.g., 2-methyl-3-buten-2-ol, MBO232) and oxygenated monoterpenes (e.g., linalool). These compounds are highly reactive toward the major atmospheric oxidants: hydroxyl radicals (OH), ozone (O_3), nitrate radicals (NO_3), and chlorine atoms (Cl), leading to very short atmospheric lifetimes (i.e., a few hours or less).[1] These oxidation processes have been shown to produce secondary pollutants such as ozone and oxygenates impacting the tropospheric chemical composition.[2−7] In order to understand and assess the role of unsaturated alcohols and biogenic volatile organic compounds (BVOCs) in atmospheric chemistry, it is important to not only quantify their emissions and atmospheric abundance but also understand their atmospheric oxidation processes.

In this work, the atmospheric degradation of three unsaturated alcohols has been investigated: linalool (3,7-dimethylocta-1,6-dien-3-ol) $[(CH_3)_2C{=}CHCH_2CH_2C(OH)(CH_3)CH{=}CH_2]$, 6-methyl-5-hepten-2-ol $[(CH_3)_2C{=}CHCH_2CH_2CH(OH)CH_3]$, and 3-methyl-1-penten-3-ol

Special Issue: A. R. Ravishankara Festschrift

Received: November 25, 2011
Revised: February 7, 2012
Published: February 8, 2012

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[$CH_2{=}CHC(OH)(CH_3)CH_2CH_3$]. It has been reported that linalool is emitted from vegetation, especially from needles of conifers *Pinus pinea*[8] and *Pinus halepensi*[9] in the Mediterranean area and Valencia orange blossoms.[10] A mixing ratio of around 10 ppt of linalool has been reported recently at Blodgett Forest.[11] 6-Methyl-5-hepten-2-ol has been detected in numerous fruits,[12,13] and is present in significant amounts in raspberry cultivar.[14] To the best of our knowledge, no biological source of 3-methyl-1-penten-3-ol has been reported; however, it has been used in metal nanoparticle technology for particle encapsulation.[15] Investigations of the mechanisms for the oxidation of 6-methyl-5-hepten-2-ol [$(CH_3)_2C{=}CHCH_2CH_2CH(OH)CH_3$] and 3-methyl-1-penten-3-ol [$CH_2{=}CHC(OH)(CH_3)CH_2CH_3$] may also be important, since these molecules have structural features in common with linalool [$(CH_3)_2C{=}CHCH_2CH_2C(OH)(CH_3)CH{=}CH_2$]. Hence, the mechanisms for their oxidation could be useful in elucidating the reaction pathways for the OH and O_3 initiated oxidation of linalool.

However, no data on the oxidation of 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol have been reported, and a limited number of kinetic, product distribution, and aerosol formation studies on the reactions of OH and O_3 with linalool have previously been reported.[2,3,16−26] To our knowledge, for the OH reaction, no experiment has been conducted in the absence of NO_X. The present paper reports kinetic and product studies on the reactions of O_3 and OH radicals (NO_X-free conditions) with linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol. In addition, the yields of aerosol formation from these reactions have also been determined in this work.

2. EXPERIMENTAL METHODS

The experiments have been performed using three atmospheric simulation chambers: the EUPHORE facility (CEAM-Valencia, Spain) and two different chambers (7300 and 200 L) at ICARE (CNRS-Orléans, France). The rate coefficients for the reactions of O_3 with the three compounds together with the rate coefficients for the reactions of OH with 3-methyl-1-penten-3-ol and 6-methyl-5-hepten-2-ol were measured using the ICARE 7300 L chamber, while the 200 L chamber was employed for the kinetic study of OH with linalool. The mechanistic study of the O_3-initiated oxidation of 6-methyl-5-hepten-2-ol was conducted at EUPHORE, while the O_3- and OH-initiated oxidation of linalool and 3-methyl-1-penten-3-ol were performed using the 7300 L ICARE chamber.

7300L ICARE Chamber. Experiments were carried out at room temperature and 760 Torr of purified air (<5% relative humidity). The chamber, made of Teflon foil, has been previously described elsewhere.[27] It is covered by a black opaque curtain in order to work in the dark for ozone reaction studies and is equipped with 14 lamps with a wavelength of 254 nm in order to perform OH-initiated reaction experiments (UV-A T-40 L, 40W, Viber Lourmat). Rapid mixing of reactants was ensured with two fans made of Teflon during all the experimental runs. After each experiment, the chamber was flushed with purified air (flow of around 100 L min^{-1}) in order to purge the remaining chemicals from the system. For the introduction of compounds in the liquid state at room temperature, a known volume of reactant was introduced into an impinger (gently heated when necessary) and further driven into the chamber by a stream of purified air. Gaseous compounds were introduced using a calibrated cylinder (0.9 L) connected to two pressure sensors (0−10 Torr and 0−100 Torr, MKS Baratron). Reactants were monitored using an in situ Fourier transform infrared spectrometer (FT-IR, Nicolet 5700 Magna), coupled to a White-type mirror system (optical paths: 129 and 148 m). The instrument was operated in the mid-IR region (4000−650 cm^{-1}). Spectra were recorded by coadding 130 interferograms within 5 min at a resolution of 1 cm^{-1}. The alcohols and reference compounds concentrations were determined using calibrated reference spectra. Temperature and relative humidity data are recorded by a combined sensor. Ozone was generated using an electric discharge on a flow of oxygen (O_2, Air liquide), which was capable of a rapid introduction of ozone into the chamber. Ozone concentration was continuously measured by a monitor (Thermo Environment 49C or Horiba APOA-360) based on its ultraviolet absorption at 254 nm. A measurement point was obtained at least every 10 s. Secondary organic aerosols (SOAs), formed in the reactions of ozone and OH radicals with the unsaturated alcohols, were also monitored over the course of the reactions using a scanning mobility particle sizer (SMPS, model TSI 3080). The SMPS consists of a differential mobility analyzer (DMA, model TSI 3081) and condensation nuclei counter (CNC, model TSI 3022). The sample flow was fixed at 0.2 L min^{-1}, and the size distribution of the particles formed was monitored during all the experiments. The particle size diameter ranged from 20 to 1000 nm and was acquired every 5 min. Measurements started around 1 h before each experiment in order to characterize particle background in the chamber. Statistical correction for multiple charges was applied to the measured size distribution. The density of particles was assumed to be 1 g cm^{-3}.

200L ICARE Chamber. The 200 L FEP Teflon chamber was surrounded by six lamps (Sylvania, G30W) with irradiation centered at 254 nm. The chamber was suspended in a wooden box with internal faces covered by aluminum foil. Reactants were introduced into the Teflon bag by streaming purified air through a calibrated bulb (579 mL). Hydrogen peroxide was used as the source of OH radicals, and introduced by liquid injection into a stream of purified air flowing directly into the chamber. A gas chromatograph, coupled to a flame ionization detector (GC-FID, Star 3600 CX, Varian), was used to determine the concentration of reactants in the chamber. Chromatographic separations were performed with a DB-1 capillary column (J&W Scientific, 30 m, 0.32 mm, and 5 μm film) operated at various temperatures from 353 to 508 K.

EUPHORE Chamber. Gas-phase product investigations of the ozonolysis of 6-methyl-5-hepten-2-ol were performed at the EUropean PHOtoREactor (EUPHORE), the large outdoor simulation chamber in Valencia, Spain. A detailed description of the EUPHORE facility can be found elsewhere.[28−31] It consists of an approximately 200 m^3 hemispherical chamber made of FEP Teflon. Two fans are interfaced into the chamber, which ensure homogeneous mixing of the air. The chamber is equipped with an in situ FT-IR spectrometer (Magna 550) coupled to a White-type mirror system with an optical path of 553.5 m. Infrared spectra were recorded every 5 min coadding 280 spectra with a resolution of 1 cm^{-1}. The reactant and gas phase products were also monitored by gas chromatography using several different detectors (photoionization detector (PID), electron capture detector (ECD), and mass spectrometer detector (MS)). Carbonyl compounds were sampled on 2,4-dinitrophenylhydrazine (DNPH) cartridges, and the derivatives were analyzed by high-performance liquid chromatography with UV detector (HPLC-UV). Ozone was measured using a monitor

employing UV absorption. Particle formation was monitored by an SMPS and a tapered elemental oscillating microbalance (TEOM).

While the OH reaction rate coefficients have been determined only by the relative rate method, those for the reactions of ozone were measured using both relative and absolute rate methods. In a conventional relative rate method, the values of the rate coefficients are determined by following the parallel decays of the alcohols and the organic reference compounds. Loss of the alcohols and the reference compounds occur in the following reactions:

$$\text{Alcohol} + \text{OH}/\text{O}_3 \rightarrow \text{Products} \quad k_{\text{Alcohol}}$$

$$\text{Reference} + \text{OH}/\text{O}_3 \rightarrow \text{Products} \quad k_{\text{Ref}}$$

k_{Alcohol} and k_{Ref} are the rate coefficients of the reactions of OH and ozone with the studied alcohols and reference compounds, respectively. Assuming that the unsaturated alcohols and reference organic compounds are removed only by reaction with OH or ozone and by dilution processes, it can be shown that

$$\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_{\text{L}}(\text{Alcohol}) \times t = k_{\text{Alcohol}}/k_{\text{Ref}}(\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_{\text{L}}(\text{Ref}) \times t)$$

where $[\text{Alcohol}]_0$, $[\text{Ref}]_0$, $[\text{Alcohol}]_t$ and $[\text{Ref}]_t$ are the concentrations (in molecules cm^{-3}) of the unsaturated alcohol and the reference organic compound at times t_0 and t, respectively. k_{Alcohol} and k_{Ref} are the rate coefficients for the reactions of OH radicals or ozone with the unsaturated alcohol and reference compound, respectively. To take into account the decay of substrate and reference compounds due to dilution and wall loss (no photolysis of these compounds was observed under our experimental conditions), the terms $k_{\text{L}}(\text{Alcohol})$ and $k_{\text{L}}(\text{Ref})$ are introduced into the equation. These terms were determined from the pseudo-first-order decay of the alcohol and reference compounds in the absence of any oxidants. The quoted error attributed to the determined rate coefficient k_{Alcohol} results from one standard deviation (1σ) from the slope of the plot of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_{\text{L}}(\text{Alcohol}) \times t$ against $\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_{\text{L}}(\text{Ref}) \times t$ and the uncertainty in the rate coefficient of the reference compound. Butyl vinyl ether, isoprene, cyclohexene, 3-methyl-3-buten-1-ol, and propene were selected as reference organic compounds. In the study using the 7300 L chamber, the reference compounds were monitored by FT-IR spectroscopy over the following wavenumber ranges: cyclohexene, 3054−3013 cm^{-1}; propene, 966−872 cm^{-1}; butyl vinyl ether, 1239−1168 cm^{-1}; 3-methyl-3-buten-1-ol, 3118−3055 cm^{-1}.

In the absolute kinetic studies of the reactions of ozone with unsaturated alcohols, the concentrations of alcohols were in excess over those of ozone, typically $[\text{Alcohol}]_0 = (1.35-12.8) \times 10^{13}$ and $[\text{Ozone}]_0 = (0.69-13.9) \times 10^{12}$ (in molecules cm^{-3}). Under pseudo-first-order conditions, ozone decay follows the following kinetic law:

$$[\text{O}_3]_t = [\text{O}_3]_0 e^{-k't} \quad \text{where} \quad k' = k[\text{Alcohol}]_0 + k'_0$$

with k representing the rate coefficient for the reaction of O_3 with the three alcohols investigated, and k'_0 being the first-order rate coefficient for O_3 removal in the absence of alcohol. Loss of O_3 also occurs by dilution and at the wall of the chamber. By repeating the experiments at different initial concentrations of alcohol, a plot of the pseudo-first-order rate coefficient ($k'-k'_0$) versus initial alcohol concentration $[\text{Alcohol}]_0$ was obtained. The slope of the plot gives the rate coefficient for the reaction of O_3 with the alcohol k. The quoted error in the obtained rate coefficient corresponds to one-standard deviation (1σ) from the slope.

Production of aerosols was observed from the reaction of unsaturated alcohols with both ozone and OH radicals. Experiments were carried out at room temperature and a relative humidity <5%. SOA mass yields were estimated from the particle volumetric yields assuming an aerosol density of 1 g cm^{-3}. The residual particle concentration prior to the start of the reactions was also measured (N < 50 cm^{-3} and M_0 < 0.1 $\mu\text{g m}^{-3}$). After nucleation, the particle number slowly decreased through coagulation or/and wall loss on the Teflon film chamber wall. Particle volume concentration increased over the course of the reaction and decreased due to wall losses at the end of the reaction. Concentration−time profiles of the aerosols were corrected for wall loss using the measured aerosol decay rates at the end of the reaction. SOA mass yields (Y) were estimated from the formed aerosol mass concentration (M_0 in $\mu\text{g m}^{-3}$) and the consumed concentration of VOCs ($\Delta[\text{Alcohol}]$ in $\mu\text{g m}^{-3}$) ratio:

$$Y = \frac{M_0}{\Delta[\text{Alcohol}]}$$

The quoted error on the SOA mass yields originates from the uncertainties of the values of M_0 and $\Delta[\text{Alcohol}]$, estimated to one-standard deviation (1σ).

3. CHEMICALS

The commercial source of chemicals used in this work and their stated purities are as follows: linalool (97%, Acros Organics and Alfa Aesar), 6-methyl-5-hepten-2-ol (98%, Alfa Aesar), 3-methyl-1-penten-3-ol (98%, Alfa Aesar), propene (99.5%, Air Liquide), cyclohexene (≥99.5%, Fluka), butyl vinyl ether (98%, Sigma Aldrich), 3-methyl-3-buten-1-ol (97%, Sigma Aldrich), propyl vinyl ether (99%, Sigma Aldrich), hydrogen peroxide solution (50% in water, Sigma Aldrich), cyclohexane (≥99.5%, Sigma Aldrich) and di-*n*-butylether (≥99%, Sigma Aldrich).

4. RESULTS AND DISCUSSION

4.1. Reaction with Ozone. *Kinetic Measurements.* Examples of pseudo-first-order decays of ozone as a function of reaction time for different concentrations of linalool are given in Figure 1. The reaction rate coefficients were derived from the least-squares data fits of plots of ($k'-k'_0$) against ($[\text{Alcohol}]_0$). Figure 2a−c displays plots of ($k'-k'_0$) versus the alcohol concentrations for the reactions of ozone with linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol, respectively. To avoid any complications due to the generation of OH radicals in the chemical system, most runs were conducted in the presence of an OH scavenger: cyclohexane (7.8×10^{15} molecules cm^{-3}) for 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol, and di-*n*-butylether ($(1.2 - 2.4) \times 10^{15}$ molecules cm^{-3}) for linalool. The rate coefficients for the reactions of cyclohexane and di-*n*-butylether with OH radicals are $k = (6.97 \pm 1.39) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[32] and $k = (2.80 \pm 0.42) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[1] at 298 K, respectively. During the absolute rate method experiments, the ozone monitor initially showed slightly negative interferences in the presence of linalool and 6-methyl-5-hepten-2-ol. In these experiments, injection of ozone was performed when the ozone monitor

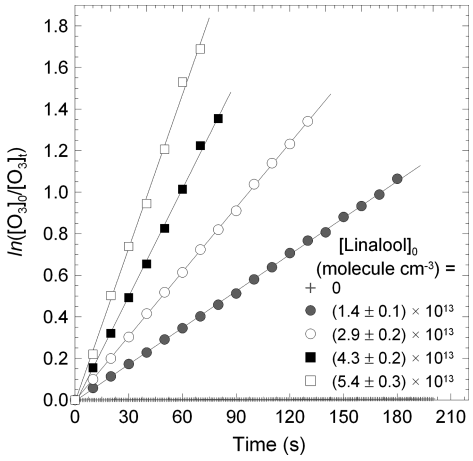

Figure 1. Reaction of ozone with linalool (absolute rate method): examples of pseudo-first-order ozone decays as a function of reaction time in the presence of different concentrations of linalool.

signal was stable, typically 15 min after the introduction of the alcohol. Due to the low vapor pressure of unsaturated alcohols, ozone was introduced after the compound. Therefore, the ozone leakage first-order rate coefficient was determined in a series of separate experiments. The average rate coefficient for ozone loss was $k_0 = (2.5 \pm 0.2) \times 10^{-5}\ s^{-1}$. The rate coefficients (in $cm^3\ molecule^{-1}\ s^{-1}$) obtained for the reactions of O_3 with the three alcohols at 296 ± 3 K in 760 Torr of purified air are as follows:

$$\text{linalool} + O_3 \rightarrow \text{Products} \quad k = (4.1 \pm 0.4) \times 10^{-16}$$

$$\text{6-methyl-5-hepten-2-ol} + O_3 \rightarrow \text{Products} \quad k = (3.8 \pm 0.6) \times 10^{-16}$$

$$\text{3-methyl-1-penten-3-ol} + O_3 \rightarrow \text{Products} \quad k = (5.4 \pm 0.2) \times 10^{-18}$$

Additional experiments have been performed using the relative rate method. Propene was used as the reference for the reaction of 3-methyl-1-penten-3-ol with ozone, and butyl vinyl ether and propyl vinyl ether were used for the ozonolysis of linalool and 6-methyl-5-hepten-2-ol. Cyclohexane was added to the gas mixtures in sufficient concentration to scavenge more than 90% of the OH radicals potentially formed through the ozonolysis reactions. Preliminary experiments were carried out to determine the loss of the three unsaturated alcohols and organic references in the absence of ozone. Compounds and references were introduced into the chamber, and their temporal behaviors were observed from 30 min to 1 h in order

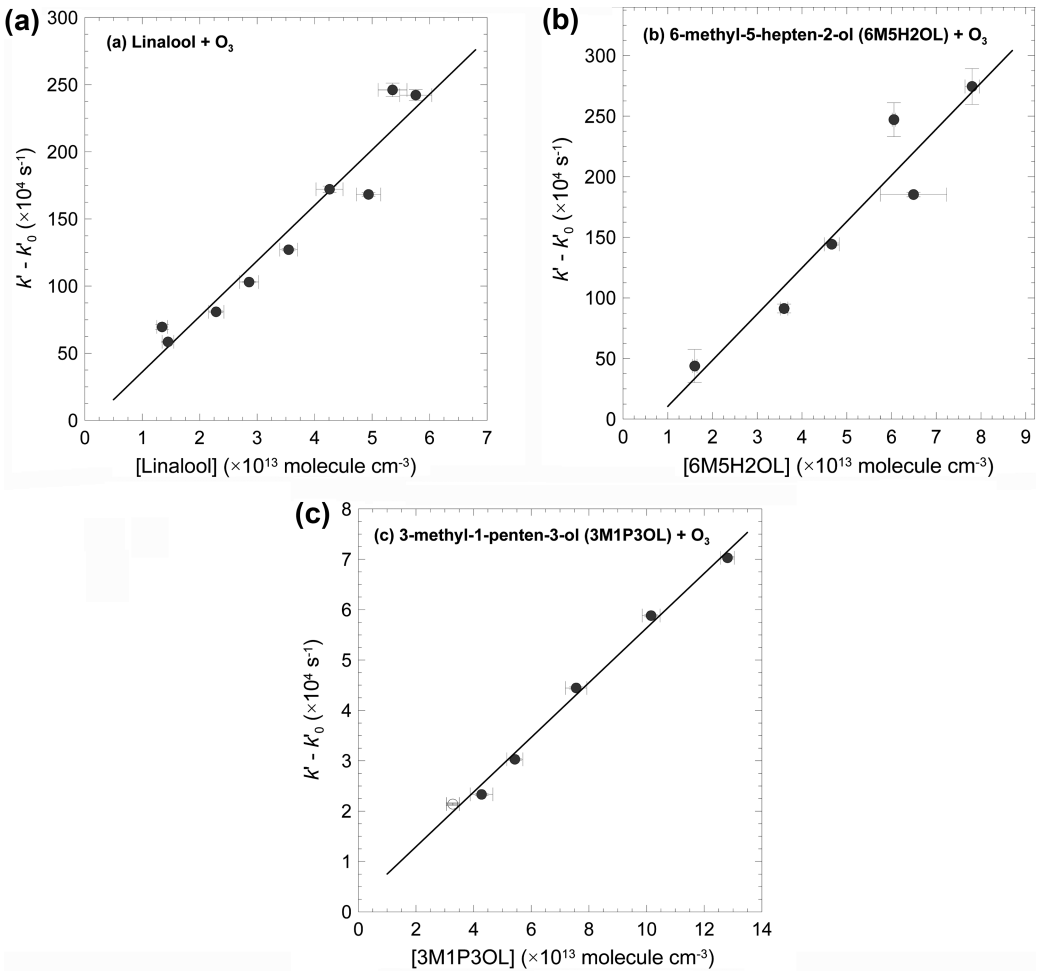

Figure 2. Reaction of O_3 with linalool (a), 6-methyl-5-hepten-2-ol (b), and 3-methyl-1-penten-3-ol (c): absolute rate kinetic data. (Experiments conducted in the presence of an excess of cyclohexane are represented with filled circles, while that conducted without cyclohexane is showed with the open symbol.)

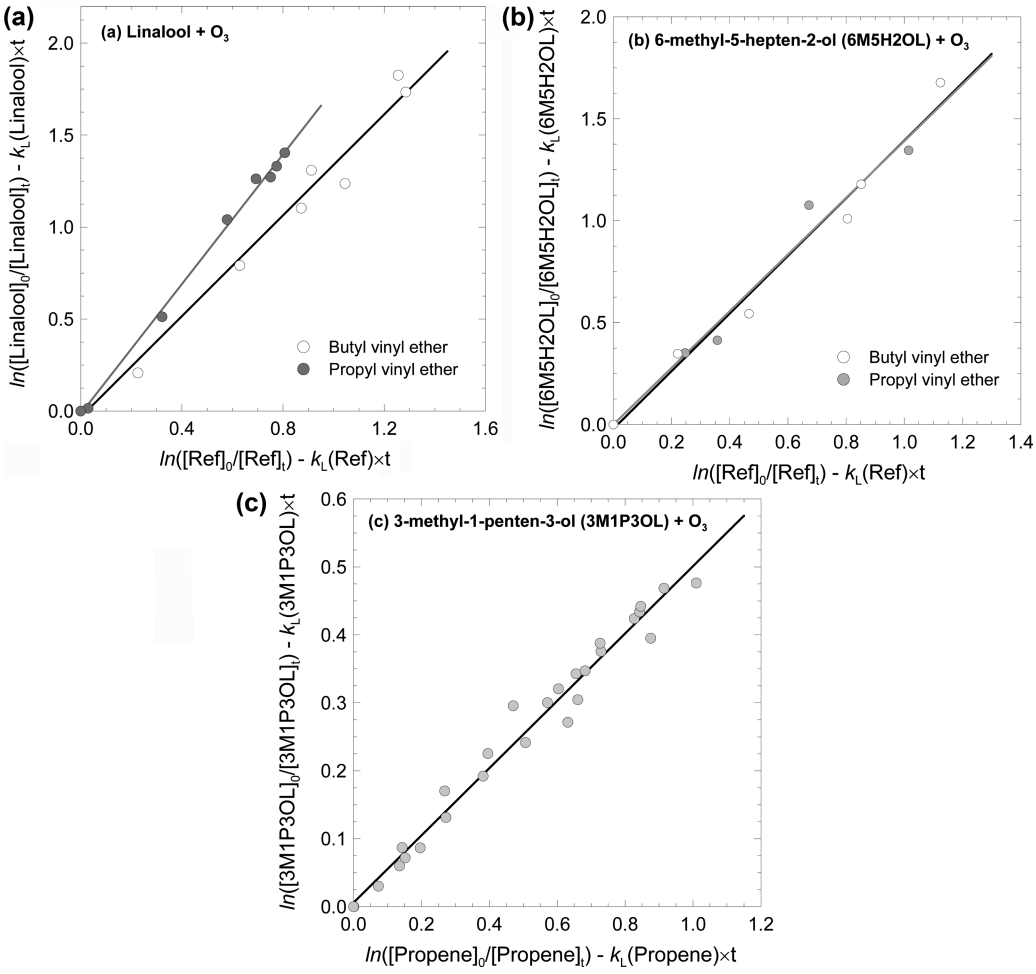

Figure 3. Reaction of O_3 with linalool (a), 6-methyl-5-hepten-2-ol (b), and 3-methyl-1-penten-3-ol (c): relative rate kinetic data using butyl vinyl ether, propyl vinyl ether, and propene as organic references.

Table 1. Reactions with O_3, Relative Rate Method: Summary of the Experimental Conditions and Results Obtained at Room Temperature in 760 Torr of Purified Air and in the Presence of an Excess of Cyclohexane

alcohols	reference	no. of runs	T (K)	$(k/k_{ref.} \pm 1\sigma)$	$(k \pm 1\sigma)$ (cm^3 molecule^{-1} s^{-1})
linalool	butyl vinyl ether	2	295.0 ± 0.3	1.38 ± 0.07	(4.0 ± 0.5) × 10^{-16}
	propyl vinyl ether	1	295.7 ± 0.1	1.77 ± 0.04	(4.3 ± 0.8) × 10^{-16}
				k = (4.1 ± 1.0) × 10^{-16} cm^3 molecule^{-1} s^{-1}	
6-methyl-5-hepten-2-ol	butyl vinyl ether	2	300.9 ± 0.3	1.41 ± 0.08	(4.1 ± 0.5) × 10^{-16}
	propyl vinyl ether	2	301.8 ± 0.1	1.39 ± 0.10	(3.3 ± 0.8) × 10^{-16}
				k = (3.7 ± 1.2) × 10^{-16} cm^3 molecule^{-1} s^{-1}	
3-methyl-1-penten-3-ol	propene	3	294 ± 2	0.50 ± 0.01	(5.0 ± 0.6) × 10^{-18}
				k = (5.0 ± 0.6) × 10^{-18} cm^3 molecule^{-1} s^{-1}	

to assess their respective total loss rate coefficients via dilution and wall loss. Initial concentrations were (in 10^{13} molecules cm^{-3}) $[\text{Alcohol}]_0$ = 1.1−7.5 and $[\text{Reference}]_0$ = 1.1−5.8. Kinetic measurements commenced after the addition of ozone, and the parallel decays of the substrates and references were monitored and quantified using FT-IR spectroscopy. The duration of the runs ranged from 10 to 30 min for linalool and 6-methyl-5-hepten-2-ol and from 20 min to 1 h for 3-methyl-1-penten-3-ol. Plots of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_L(\text{Alcohol}) \times t$ versus $(\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_L(\text{Ref}) \times t)$ were linear with slopes of $k_{\text{Alcohol}}/k_{\text{ref}}$ as shown in Figure 3a−c. The initial conditions and results are listed in Table 1. Rate coefficients have been calculated using the following values for the reference compounds (in cm^3 molecule^{-1} s^{-1}): $k(\text{propene} + O_3) = (1.0 \pm 0.1) \times 10^{-17}$,[33] $k(\text{propyl vinyl ether} + O_3) = (2.4 \pm 0.4) \times 10^{-16}$, and $k(\text{butyl vinyl ether} + O_3) = (2.9 \pm 0.2) \times 10^{-16}$.[34] The rate coefficients determined (in cm^3 molecule^{-1} s^{-1}) for the three unsaturated alcohols are

$$\text{linalool} + O_3 \rightarrow \text{Products} \quad k = (4.1 \pm 1.0) \times 10^{-16}$$

$$\text{6-methyl-5-hepten-2-ol} + O_3 \rightarrow \text{Products} \quad k = (3.7 \pm 1.2) \times 10^{-16}$$

3-methyl-1-penten-3-ol + O_3 → Products

$$k = (5.0 \pm 0.6) \times 10^{-18}$$

These rate coefficients values are in good agreement with those derived from the absolute rate technique. Therefore, we recommend the average values of the rate coefficients obtained from both relative and absolute rate studies (in cm^3 $molecule^{-1}$ s^{-1}):

linalool + O_3 → Products $k = (4.1 \pm 1.0) \times 10^{-16}$

6-methyl-5-hepten-2-ol + O_3 → Products

$$k = (3.8 \pm 1.2) \times 10^{-16}$$

3-methyl-1-penten-3-ol + O_3 → Products

$$k = (5.2 \pm 0.6) \times 10^{-18}$$

No kinetic data have been reported for the reactions of O_3 with 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol, while two previous investigations on the reaction with linalool have been carried out.[16,19] The rate coefficient determined by Atkinson et al.[16] was obtained using the relative rate method, with 2-methyl-2-butene used as the reference compound. Taking k(2-methyl-2-butene + O_3) = 4.1×10^{-16} cm^3 $molecule^{-1}$ s^{-1},[33] a value of the rate coefficient for the reaction of O_3 with linalool of $k = (4.5 \pm 0.1) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} was derived, which is in very good agreement with our value of ($k = (4.1 \pm 1.0) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}). Grosjean and Grosjean[19] employed an absolute rate technique to study the reaction in which the concentration of linalool was in large excess over ozone. The authors could only report an upper limit for the rate coefficient of $k \geq (3.15 \pm 0.23) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, since the rate of ozone decay in the system was similar to the response time of the ozone monitor.

The data obtained in the present work indicate that the rate coefficients for the reactions of ozone with linalool and 6-methyl-5-hepten-2-ol are similar, while that for reaction with 3-methyl-1-penten-3-ol is around 2 orders of magnitude lower. The high reactivity of linalool and 6-methyl-5-hepten-2-ol can be explained, at least in part, by the high degree of substitution of the double bond ($-CH{=}C(CH_3)_2$) at which the reaction with ozone is expected to proceed. As expected, the low degree of substitution of the double bond ($-CH{=}CH_2$) leads to the observed reduction in reactivity of 3-methyl-1-penten-3-ol toward O_3, which is in agreement for the corresponding reaction with the structurally similar compound 2-methyl-3-buten-2-ol ($CH_2{=}CHC(CH_3)_2(OH)$) within the stated uncertainties ($k = (1.0 \pm 0.6) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}).[33]

It is of interest to note that the value of the rate coefficient for the reaction of O_3 with linalool is close to the sum of the rate coefficients for the reactions of O_3 with the other two unsaturated alcohols investigated:

$$k(\text{6-methyl-5-hepten-2-ol} + O_3) + k(\text{3-methyl-1-penten-3-ol} + O_3) \approx k(\text{linalool} + O_3)$$

The rate coefficients obtained in this work suggest that for the reaction of O_3 with linalool, attack at the $R{-}CH{=}C(CH_3)_2$ group represents around (93 ± 52)% ($k_{\text{6-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the overall reaction while the attack at the $R{-}CH{=}CH_2$ group, accounting for about (1.3 ± 0.5)% ($k_{\text{3-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). Atkinson et al.[16] and Shu et al.[3] previously proposed that 97% of the reaction with ozone proceeds by addition to the $R{-}CH{=}C(CH_3)_2$ group and only 3% proceeds by addition to the $R{-}CH{=}CH_2$ group, in agreement with the estimates from the present study.

Gas-Phase Product Studies. For each unsaturated alcohol, a set of three experiments was performed in the presence of cyclohexane as a scavenger for OH radicals. In all the experiments, the alcohol was injected first into the chamber followed by the addition of cyclohexane. Prior to the addition of ozone, the organic compounds were monitored for at least 30 min. The reactant concentrations employed were in the range of $(1.62{-}4.49) \times 10^{13}$ molecules cm^{-3} at ICARE and $(4.91{-}5.59) \times 10^{12}$ molecules cm^{-3} at EUPHORE. Figure 4 displays IR spectra obtained from the ozonolysis of linalool at different stages of the reaction. The reference spectrum of linalool is shown in panel A, while panels B and C show the IR spectra of

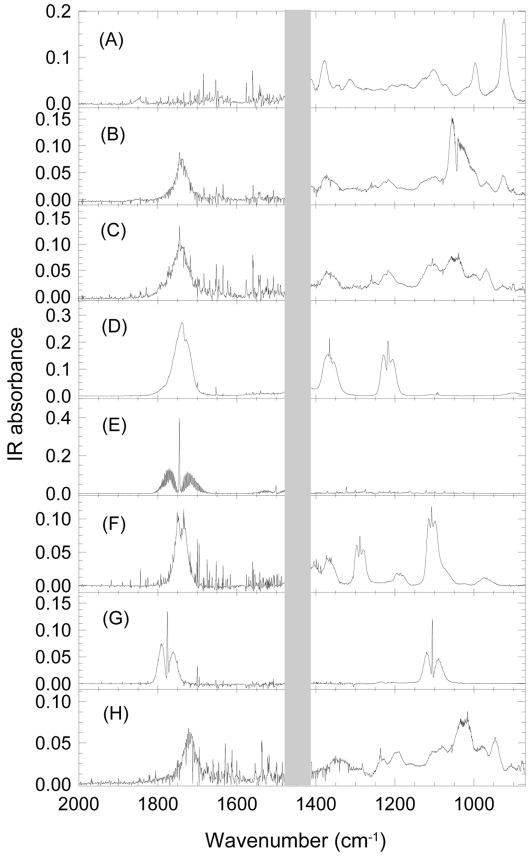

Figure 4. Reaction of linalool with O_3 (in the presence of an excess of cyclohexane). Cyclohexane was subtracted from all the IR spectra shown here. Reference IR spectrum of linalool (A); IR spectrum of a mixture of linalool and O_3 at the start of the experiment (B); IR spectrum of a mixture of linalool and O_3 after 2 h of reaction (C) (linalool and O_3 are subtracted from the global spectrum); reference IR spectra of acetone (D), formaldehyde (E), hydroxyacetone (F), and formic acid (G); IR residual spectrum after subtraction of reactants (linalool and O_3) and all identified products (major products: acetone, formaldehyde, and hydroxyacetone (and formic acid observed as a secondary minor product) (H). The gray overlap area represents IR band saturation due to the excess of cyclohexane used as OH scavenger.

linalool and O_3 at the start of the reaction and after 2 h of reaction, respectively. Panels D, E, F, and G display the IR reference spectra of acetone, formaldehyde, hydroxyacetone, and formic acid, respectively. A typical residual IR spectrum (after subtraction of the reactants and all identified products) is shown in panel H. The derived product formation yields for the reactions of ozone with the unsaturated alcohols are summarized in Tables (2−4).

Table 2. Reaction of Linalool with O_3: Gas Phase Product Yields (Cyclohexane Used as OH Scavenger)

linalool + O_3	
acetone	35 ± 6
formaldehyde	32 ± 6
hydroxyacetone	28 ± 5
carbon balance	*22 ± 4*

Table 3. Reaction of 6-Methyl-5-hepten-2-ol with O_3: Gas Phase Product Yields (Cyclohexane Used as OH Scavenger)

6-methyl-5-hepten-2-ol + O_3	
acetone[a,b]	31 ± 7
formaldehyde[a]	40 ± 10
hydroxyacetone[a]	17 ± 2
formic acid[a]	16 ± 4
methylglyoxal[c,d]	10 ± 1
4-hydroxypentanal[d,e]	34 ± 11
carbon balance	*50 ± 12*

[a]Obtained from FT-IR analysis. [b]Obtained from GC-PID analysis. [c]Obtained from GC-ECD analysis. [d]Yields of identified products measured by HPLC-UV and by GC-ECD are obtained by the consumption of 6-methyl-5-hepten-2-ol by GC-MS. [e]4-hydropentanal was quantified using 4-pentanal as a surrogate by HPLC-UV (see text).

Table 4. Reaction of 3-Methyl-1-penten-3-ol with O_3: Gas Phase Product Yields (Cyclohexane Used as OH Scavenger)

3-methyl-1-penten-3-ol + O_3	
formaldehyde	29 ± 4
carbon monoxide	8 ± 1
2-butanone	46 ± 3
carbon balance	*37 ± 2*

Products identified from the reaction of ozone with linalool were acetone (35 ± 6)%, formaldehyde (32 ± 6)%, and hydroxyacetone (28 ± 5)%. Ozonolysis of 3-methyl-1-penten-3-ol gave formaldehyde and 2-butanone as the major products with formation yields of (29 ± 4)% and (46 ± 3)%, respectively. A stoichiometric ratio of $\Delta[O_3]/\Delta$[3-methyl-1-penten-3-ol] = 1.1 ± 0.1 was obtained in the absence of cyclohexane, suggesting that the formation yield of OH radicals in the system was negligible. The products identified and quantified from the reaction of ozone with 6-methyl-5-hepten-2-ol were acetone (31 ± 7)%, formaldehyde (40 ± 10)%, hydroxyacetone (17 ± 2)%, formic acid (16 ± 4)%, and methylglyoxal (10 ± 1)%. Formation of 4-hydroxypentanal as a product of the ozonolysis was also expected; however, a sample of this compound was not commercially available, and hence it could not be positively quantified. The yield of 4-hydroxypentanal was tentatively quantified using 4-pentanal as a surrogate, which was introduced into the gas mixture at the end of the experiment. A yield of 4-hydroxypentanal of around 34% was estimated using HPLC-UV, assuming the response factor for the DNPH derivatives of both 4-pentanal and 4-hydroxypentanal were the same. In addition, cyclohexanone and cyclohexanol have also been identified as products by GC-MS, indicating the formation of OH radicals in the ozonolysis reaction.[35] Then, OH formation yield from the ozonolysis of 6-methyl-5-hepten-2-ol was derived and found to be (65 ± 20)%, which is similar to that of linalool (66 ± 10)%.[22]

To date, of the unsaturated alcohols studied in this work, only the gas-phase products from the ozonolysis of linalool have been reported.[2,3,23] Grosjean and Grosjean[2] performed experiments with a relative humidity of 50%, while the other studies were conducted with relative humidities below 10%. The acetone yield (35 ± 6)% obtained in this work agrees with that reported by Grosjean and Grosjean[2] [(28 ± 1)%] but is higher than that from Shu et al.[3] [(21.1 ± 2.4)%] and Lee et al.[23] [(16 ± 1)%]. The measured yield of formaldehyde [(32 ± 6)%] is in line with the previously reported values by Shu et al.[3] [(36 ± 6)%] and Lee et al.[23] [(34 ± 3)%]. Hydroxyacetone was detected as a product of the ozonolysis of linalool in this work with a yield of (28 ± 5)%. This product has not previously been observed; however, Grosjean and Grosjean[2] detected methylglyoxal as a reaction product with a yield of (11 ± 1)% following derivatization with DNHP. This product could not be resolved under our experimental conditions; however, as mentioned by Grosjean and Grosjean,[2] the reaction of hydroxyacetone and methylglyoxal with DNHP leads to the same derivative. Hence, it is possible that hydroxyacetone may interfere in the quantification of methylglyoxal. 4-Hydroxy-4-methyl-5-hexen-1-al (or 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran) has also been reported as a major product from the ozonolysis of linalool with formation yields of (85 ± 14)%,[3] and (50 ± 9)%.[23] 5-Ethenyldihydro-5-methyl-2(3*H*)-furanone and acetaldehyde were also detected as products with yields of (12.6 ± 2.5)%,[3] and (14 ± 1)%,[23] respectively.

It is well established that the reaction of ozone with unsaturated alcohols proceeds by electrophilic addition of ozone to the double bond.[36] This leads to a primary ozonide, which decomposes to an energy-rich Criegee biradical and the corresponding carbonyl compound. A mechanistic scheme for the reaction of ozone with 3-methyl-1-penten-3-ol is shown in Figure 5 based on the observed and/or expected products. This reaction proceeds by initial addition of ozone to the R−CH═CH_2 group forming an ozonide, which then rapidly decomposes to either $C_2H_5C(OH)(CH_3)CHO$ (3-hydroxy-3-methyl-1-butanal) plus the $[CH_2OO]^*$ biradical or HCHO plus the $[C_2H_5C(OH)(CH_3)CHOO]^*$ biradical. The energy-rich $[CH_2OO]^*$ biradical can either be stabilized or decomposes to form HCOOH, CO, CO_2, H_2O, H_2, and the OH radical.[37,38] The Criegee intermediate $[C_2H_5C(OH)(CH_3)CHOO]^*$, formed through channel 2, can also be either stabilized to form 3-hydroxy-3-methyl-1-butanal (channel 2a), or decomposes to form CO_2 and the $C_2H_5C(OH)(CH_3)$ alkoxy radical. This radical will rapidly react with O_2 to form 2-butanone. On the basis of the observed yield of 2-butanone, the proposed mechanism suggests that channel 2 accounts for at least 46% of the reaction of O_3 with 3-methyl-1-penten-3-ol. Thus, it appears that decomposition of the primary ozonide in channels 1 and 2 is of equivalent importance. The mechanism suggests that the yield of formaldehyde should at least be the same as that for 2-butanone. However, the formaldehyde formation yield was found to be only 29%, which indicates that either formaldehyde is removed from the system in secondary processes or there is an additional source of 2-butanone not identified in this work.

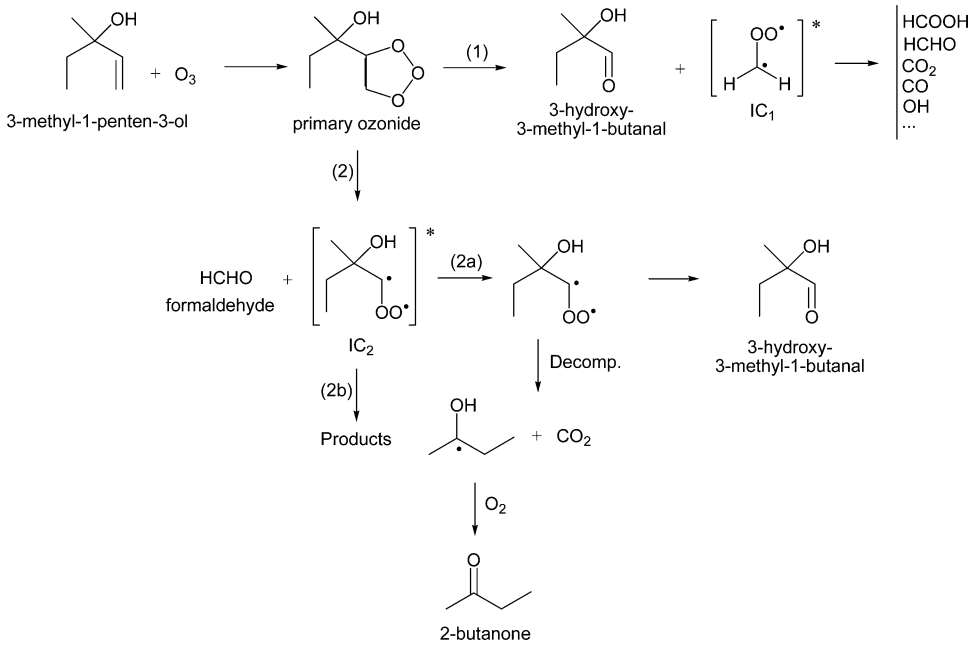

Figure 5. Reaction of 3-methyl-1-penten-3-ol with O_3: proposed mechanism scheme.

The available kinetic data suggest that the reactions of ozone with linalool and 6-methyl-5-hepten-2-ol occur mainly at the R−CH═C$(CH_3)_2$ double bond, and that addition at the R−CH═CH_2 double bond will only represent a minor pathway. Decomposition of primary ozonides can lead either to the formation of acetone and the corresponding Criegee biradical (CI_1) in channel 1, or form the biradical [$(CH_3)_2COO$]* (CI_2) and the carbonyl compounds 4-hydroxy-4-methyl-5-hexen-1-al and 4-hydroxypentanal from linalool and 6-methyl-5-hepten-2-ol, respectively. Moreover, the observed products (formaldehyde and hyroxyacetone) and the OH formation yields from the ozonolysis of linalool and 6-methyl-5-hepten-2-ol indicate that the hydroperoxide channel is an important pathway in the fate of [$(CH_3)_2COO$]* via the formation of the [$CH_3C(OOH)$═CH_2]* isomer.[39,40]

Aerosol Formation. Under our experimental conditions, the SOA mass yields from the ozonolysis of 3-methyl-1-penten-3-ol ranged from 0 to 1.9% in the absence of OH scavenger and from 0.08 to 0.3% in the presence of cyclohexane. The ozonolysis of 6-methyl-5-hepten-2-ol led to a SOA mass yield of around 2% in the absence of OH scavenger and 0.5% in the presence of cyclohexane. Linalool ozonolysis experiments showed that for reactions performed in the presence of cyclohexane, the SOA mass yields varied from 1.4% to 1.9%, while in the absence of an OH scavenger the SOA yield was approximately 10%. The SOA yields from the ozonolysis of linalool in the presence of an OH scavenger obtained in this study are in broad agreement with that of 1% reported by Lee et al.[23] In the absence of a scavenger, the 10% SOA yield determined in this work is in reasonable agreement with the value of 8% reported by Hoffmann et al.,[18] although considerably higher than the estimate of 2% obtained by Chen et al.[26] The present results show that SOA formation from the ozonolysis of the unsaturated alcohols studied is relatively low. Nevertheless, in the absence of OH scavengers, the SOA mass yield is higher than in their presence, which is in agreement with previous observations from studies on the ozonolysis of alkenes.[41−43]

4.2. Reaction with OH Radicals. *Kinetic Measurements.* OH radicals were generated through the photolysis of H_2O_2 at 254 nm. Preliminary experiments were performed in order to check the stability of the alcohols in the presence of the reference compounds and H_2O_2 in the dark. Additional tests were carried out in order to check the photostability of the organic compounds in the absence of H_2O_2. The duration of the tests ranged from 30 min to more than 1 h. The results of these experiments showed that decay of the organic compounds in the absence of H_2O_2 was negligible except for loss at the wall and by dilution. No loss other than the reaction with OH radicals has been observed for linalool and the reference compounds. The experiments on 3-methyl-1-penten-3-ol and 6-methyl-5-hepten-2-ol were conducted in the 7300 L chamber using FT-IR as the analytical tool, while the study of the reaction of linalool with OH was performed in the 200 L chamber using GC-FID for monitoring the decays of the organic compounds. The initial concentrations used in the 7300 L chamber were $[\text{Alcohol}]_0 = (2.6–4.8) \times 10^{13}$, $[\text{Reference}]_0 = (2.6–5.3) \times 10^{13}$, and $[H_2O_2]_0 = (3–4) \times 10^{14}$ molecules cm^{-3}. The initial concentrations of reactants employed in the 200 L chamber for the linalool experiments were (in molecules cm^{-3}) $[\text{Linalool}]_0 = (2.0–6.6) \times 10^{14}$, $[\text{Reference}]_0 = (2.5–6.6) \times 10^{14}$, and $[H_2O_2]_0 = (1–4) \times 10^{15}$. Experimental durations varied from 90 to 120 min. Plots of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_L(\text{Alcohol}) \times t$ against $(\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_L(\text{Ref}) \times t)$ gave good straight lines (Figure 6a−c for linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol, respectively), and the slopes provide values of the rate coefficient ratios $k_{\text{Alcohol}}/k_{\text{Ref}}$. The reference rate coefficients used to derive the rate coefficients for the reactions of OH with the three unsaturated alcohols were (in cm^3 $molecule^{-1}$ s^{-1}) butyl vinyl ether and propyl vinyl ether [$(1.1 \pm 0.1) \times 10^{-10}$],[44] isoprene [$(1.0 \pm 0.1) \times 10^{-10}$],[33] propene [$(2.9 \pm 0.3) \times 10^{-11}$],[33] cyclohexene [$(6.8 \pm 1.7) \times 10^{-11}$],[36] and 3-methyl-3-buten-1-ol [$(9.4 \pm 0.4) \times 10^{-10}$][45].

The experimental conditions and the values obtained for $k_{\text{Alcohol}}/k_{\text{Ref}}$ are listed in Table 5. The rate coefficients for the studied reactions are taken as the average of different

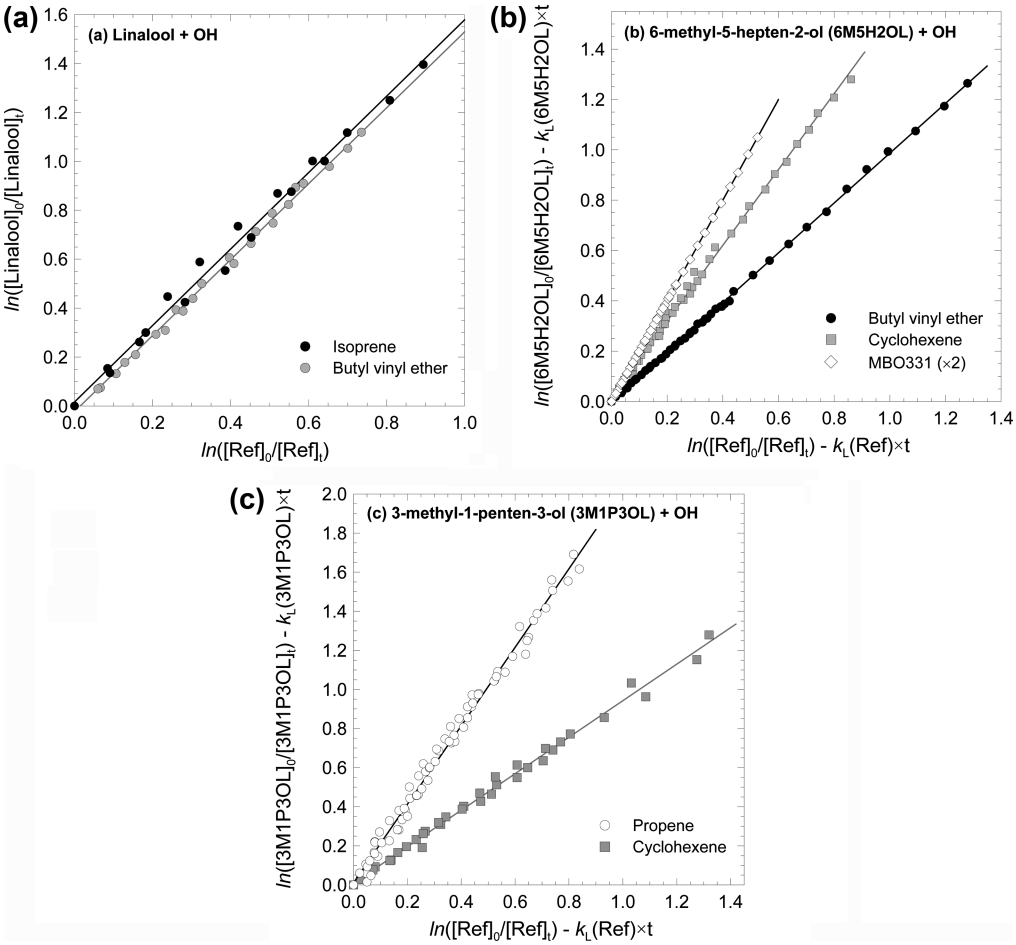

Figure 6. Reaction of OH radicals with linalool (a), 6-methyl-5-hepten-2-ol (b), and 3-methyl-1-penten-3-ol (c): relative rate kinetic data using butyl vinyl ether, isoprene, 3-methyl-3-buten-1-ol (MBO331), cyclohexene, and propene as organic references.

Table 5. Reactions with OH Radicals, Relative Rate Method: Summary of the Experimental Conditions and Results Obtained at Room Temperature in 760 Torr of Purified Air

alcohols	reference	no of runs	T (K)	$(k/k_{ref.} \pm 1\sigma)$	$(k \pm 1\sigma)$ (cm^3 molecule^{-1} s^{-1})
linalool	butyl vinyl ether	2	298 ± 1	1.57 ± 0.05	1.73 ± 0.21
	isoprene	2	298 ± 1	1.61 + 0.09	1.61 ± 0.25
				$k = (1.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}	
6-methyl-5-hepten-2-ol	butyl vinyl ether	2	294.9 ± 0.7	0.97 ± 0.02	1.07 ± 0.12
	cyclohexene	2	293.4 ± 0.5	1.52 ± 0.06	1.03 ± 0.30
	3-methyl-3-buten-1-ol	2	294.8 ± 0.9	1.05 ± 0.05	0.99 ± 0.09
				$k = (1.0 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}	
3-methyl-1-penten-3-ol	propene	2	296.2 ± 0.7	2.1 ± 0.1	0.61 ± 0.09
	cyclohexene	2	295.7 ± 0.7	0.94 ± 0.03	0.64 ± 0.18
				$k = (6.2 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}	

measurements leading to (at 296 ± 4 K, 760 Torr of purified air, and in cm^3 molecule^{-1} s^{-1})

$$\text{linalool} + \text{OH} \rightarrow \text{Products} \quad k = (1.7 \pm 0.3) \times 10^{-10}$$

$$\text{6-methyl-5-hepten-2-ol} + \text{OH} \rightarrow \text{Products} \quad k = (1.0 \pm 0.3) \times 10^{-10}$$

$$\text{3-methyl-1-penten-3-ol} + \text{OH} \rightarrow \text{Products} \quad k = (6.2 \pm 1.8) \times 10^{-11}$$

The quoted errors were estimated from the least-squares analysis of the relative rate data. In addition, two runs were conducted in the 7300 L chamber (using FT-IR for analysis) to measure the decay rate of linalool relative to that of 6-methyl-5-hepten-2-ol for reaction with OH radicals. The experimental result was k(linalool + OH)/k(6-methyl-5-hepten-2-ol + OH) = 1.4 ± 0.2, which is in reasonable agreement with the rate coefficient ratios determined in independent measurements (1.7 ± 0.8).

In this work, we report the first measurements of the rate coefficients for reaction of OH with 3-methyl-1-penten-3-ol and

6-methyl-5-hepten-2-ol. To our knowledge, this work is the third determination of the rate coefficient of the reaction of linalool with OH radicals.[16,21] The rate coefficient reported for the reaction of OH with linalool by Atkinson et al.[16] was performed using a relative rate method with isoprene as the reference compound. On the basis of the IUPAC recommendation[33] for k(isoprene + OH) = $(1.0 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, a value of k(linalool + OH) = $(1.57 \pm 0.20) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} was derived from the rate data in reasonable agreement with the value determined in this study. The measurement of Bernhard and Simonich[21] was also obtained using the relative rate method with styrene as the reference compound. Taking k(styrene + OH) = $(5.8 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[46] leads to a value (k(linalool + OH) = $(2.15 \pm 0.58) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is within the stated uncertainties of the rate coefficient determined in this work.

The rate coefficients determined for the reaction of OH with 3-methyl-1-penten-3-ol ($k = (6.2 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) is around 2 times higher than that estimated by the structure−activity relationship (SAR) method ($k = 2.95 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).[47,48] However, it is in line with the reported rate coefficient for the reaction of OH with the structurally similar compound 2-methyl-3-buten-2-ol ($CH_2{=}CHC(CH_3)_2(OH)$, $k = 6.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298).[33] The measured rate coefficient for the OH reaction with 6-methyl-5-hepten-2-ol ($k = (1.0 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) is very close to that calculated from the SAR method ($k = 9.89 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).

The kinetic data reported in this work show that (within the stated uncertainties)

$$k(\text{6-methyl-5-hepten-2-ol} + \text{OH}) + k(\text{3-methyl-1-penten-3-ol} + \text{OH}) \approx k(\text{linalool} + \text{OH})$$

in a similar manner to that found for the O_3 kinetic studies.

The reactions of the unsaturated alcohols with OH radicals proceed mainly by addition to the >C=C< double bond system. The kinetic data indicate that the sum of the rate coefficients for reaction of OH with 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol is close to that for reaction with linalool. Hence, the double bond in each of these molecules exhibits virtually the same reactivity in linalool as they have in the individual molecules. Thus, it is possible to calculate that for the reaction of OH radicals with linalool, attack of the OH radical at the $R{-}CH{=}C(CH_3)_2$ group represents around $(59 \pm 18)\%$ ($k_{\text{6-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the total reaction while addition of OH to the $R{-}CH{=}CH_2$ group is estimated to be around $(36 \pm 6)\%$ ($k_{\text{3-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). Calculations using the SAR method[47,48] suggest that OH addition at the $R{-}CH{=}C(CH_3)_2$ and $R{-}CH{=}CH_2$ groups will represent 74% and 22%, respectively, of the overall reaction.

Gas Phase Product Studies. The products of the reactions of OH radicals with the unsaturated alcohols at room temperature and 760 Torr of air were monitored using FT-IR spectroscopy. The photolysis of H_2O_2 at 254 nm was used to generate OH radicals. Reaction mixtures consisted of $(1.2{-}9.1) \times 10^{13}$ molecules cm^{-3} of unsaturated alcohols and $(0.32{-}5.7) \times 10^{14}$ molecules cm^{-3} of H_2O_2. A set of three experiments was performed for each unsaturated alcohol. The products of the reactions have been assigned using IR reference spectra when available. Gas phase formation yields for the oxidation products were obtained after correction of their concentration time-profiles for dilution and for loss by secondary reactions with OH radicals. The observed products from the three unsaturated alcohols and their corresponding reaction rate coefficients with OH (in cm^3 molecule^{-1} s^{-1}) are the following: formaldehyde (8.5×10^{-12}), formic acid (4.5×10^{-13}), carbon monoxide (2.8×10^{-12}), glycolaldehyde (8×10^{-12}), 2-butanone (1.2×10^{-12}), methanol (9×10^{-13}), acetone (1.8×10^{-13}) and 6-methyl-5-hepten-2-one (1.57×10^{-10}). These rate coefficient values were taken from the IUPAC recommendation,[33] except for 6-methyl-5-hepten-2-one, which is from Smith et al.[49] Corrections of concentration time-profiles of the oxidation products formed have been applied according to the formula given by Atkinson et al.[50] Preliminary tests were conducted in order to observe the behavior of the unsaturated alcohols in the absence of any oxidants and possible oxidation products that might be formed. The results showed that under these conditions, consumption of the unsaturated alcohols was negligible. Figure 7 shows the IR spectra

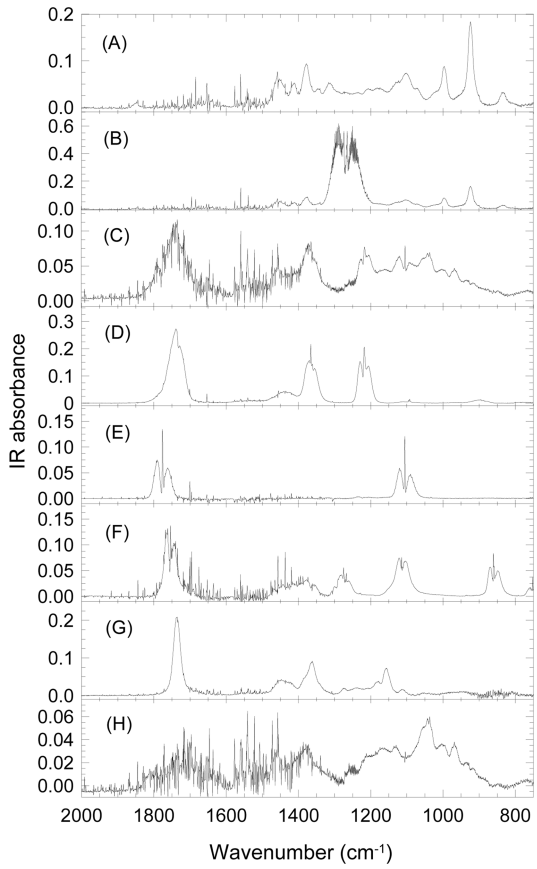

Figure 7. Reaction of linalool with OH (H_2O_2 used as OH precursor): Reference IR spectra of linalool (A); IR spectrum of mixture linalool and H_2O_2 at the start of the experiment (B); IR spectrum of a mixture of linalool and H_2O_2 after 4 h reaction (C) (linalool and H_2O_2 are subtracted from the global spectrum); reference IR spectra of acetone (D), formic acid (E), glycolaldehyde (F), and 6-methyl-5-hepten-2-one (G); IR residual spectrum after subtraction of reactants (linalool and H_2O_2) and all identified products (major products: acetone, formic acid, glycolaldehyde, and 6-methyl-5-hepten-2-one) (H).

of linalool (panel A), and a mixture of linalool and H_2O_2 at the start of the reaction (panel B). Panel C shows the IR spectrum after 4 h of reaction (linalool and H_2O_2 subtracted from the IR global spectrum). The reference spectra of acetone, formic acid, glycolaldehyde, and 6-methyl-5-hepten-2-one are displayed in the

panels D, E, F, and G, respectively. Panel H shows the residual spectrum after subtraction of reactants and all identified products.

Due to secondary reactions, the yields of gas phase products do not scale linearly with the loss of linalool over the whole experimental time. Therefore, the yields of products were obtained by plotting the gas phase product concentrations versus the linalool consumption in the early stages of the reaction, as shown in Figure 8. The molar product yields were derived from the least-squares analysis of the data and are summarized in Tables (6−8). The major products identified from the OH-initiated reaction of linalool were acetone (34 ± 1)%, glycolaldehyde (14 ± 1)%, and 6-methyl-5-hepten-2-one (10 ± 2)%. The indicated errors arise from the average of yields obtained from the three individual experiments. For the reaction of OH with 6-methyl-5-hepten-2-ol, acetone was identified as the major product with a yield of (21 ± 2)%. Other minor products identified in the system were formic acid (4.2 ± 0.7)%, formaldehyde (0.7 ± 0.4)%, and carbon monoxide (1.2 ± 0.6)%. The OH-initiated oxidation of 3-methyl-1-penten-3-ol produced 2-butanone (41 ± 6)% and glycolaldehyde (30 ± 4)% as major products with formic acid (2.2 ± 0.9)%, formaldehyde (9 ± 4)%, and carbon monoxide (2.5 ± 0.3)% as minor products.

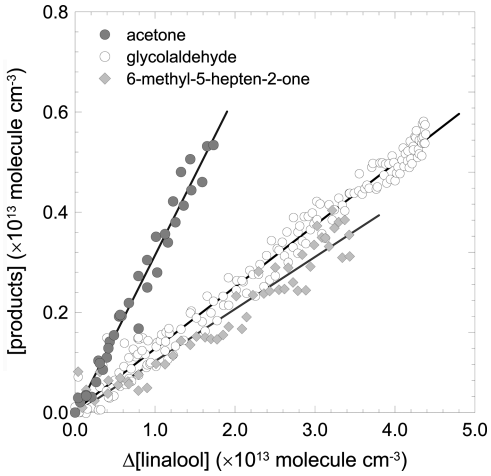

Figure 8. Reaction of linalool with OH (H_2O_2 used as OH precursor): gas phase product yields.

Table 6. Reaction of Linalool with OH Radicals: Gas Phase Product Yields (H_2O_2 Used as OH Precursor)

linalool + OH	
acetone	34 ± 1
glycolaldehyde	14 ± 1
6-methyl-5-hepten-2-one	10 ± 2
formic acid	5 ± 2
formaldehyde	2.8 ± 0.4
carbon monoxide	2.1 ± 0.8
carbon balance	*22 ± 2*

Table 7. Reaction of 6-Methyl-5-hepten-2-ol with OH Radicals: Gas Phase Product Yields (H_2O_2 Used as OH Precursor)

6-methyl-5-hepten-2-ol + OH	
acetone	21 ± 2
formic acid	4.2 ± 0.7
carbon monoxide	1.2 ± 0.6
formaldehyde	0.7 ± 0.4
Carbon balance	*8 ± 1*

Table 8. Reaction of 3-Methyl-1-penten-3-ol with OH Radicals: Gas Phase Product Yields (H_2O_2 Used as OH Precursor)

3-methyl-1-penten-3-ol + OH	
2-butanone	41 ± 6
glycolaldehyde	30 ± 4
formaldehyde	9 ± 4
carbon monoxide	2.5 ± 0.3
formic acid	2.2 ± 0.9
carbon balance	*40 ± 6*

A number of product studies on the OH radical-initiated oxidation of linalool have been reported; however, the previous studies were carried out in the presence of NO_X.[3,17,24] Therefore, this work reports for the first time the yields of products from the OH-initiated oxidation in the absence of NO_X. The OH initiated oxidations of 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol have not previously been reported.

The kinetic data leads to the prediction that the addition of OH to the ($R-CH{=}C(CH_3)_2$) group is likely to dominate over reaction at ($R-CH{=}CH_2$) with a ratio of around 59%/36%. The proposed reaction schemes following OH addition at the $R-CH{=}CH_2$ and $R-CH{=}C(CH_3)_2$ sites in linalool are shown in Figure 9a,b, respectively. 6-Methyl-5-hepten-2-one and glycolaldehyde are expected to be formed following OH attack at the $={CH_2}$ position of the $R-CH{=}CH_2$ double bond as shown in reaction channel 1 of Figure 9a. Addition of OH to the RCH= position of the double bond leads to the generation of formaldehyde and 2,6-dimethyl-2-hydroxy-5-hepten-1-one (channel 2). The low yield of HCHO (2.8%) indicates that OH radical addition at the $={CH_2}$ position (channel 1) is dominant. This result is consistent with the observation that the addition of radical species normally occurs at the least substituted carbon atom of a double bond in an alkene, and is in agreement with the low HCHO yield reported previously by Shu et al.[3] Addition of the OH radical to the $R-CH{=}C(CH_3)_2$ group of linalool is expected to produce acetone and its coproduct 4-hydroxy-4-methyl-5-hexen-1-al (or 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran) by both channels 1 and 2 (Figure 9b). The yield of 4-hydroxy-4-methyl-5-hexen-1-al was not quantified, since a reference spectrum of this compound was not available. Its formation yield has been estimated at (75 ± 10)% by Lee et al.,[24] (46 ± 11)% by Shu et al.,[3] and in the range 18−43% by Calogirou and Kotzias[17] in studies performed in the presence of NO_X.

Acetone is formed from decomposition of the alkoxy radical generated following the addition of OH to either carbon atom of the $R-CH{=}C(CH_3)_2$ double bond in linalool, while glycolaldehyde is the major product generated by addition of OH to the $R-CH{=}CH_2$ group (Figure 9b,a, respectively). Assuming that the peroxy radicals produced in the reaction of OH with linalool are quantitatively converted to the corresponding alkoxy radicals, the ratio of the yields of acetone (34%) to glycolaldehyde (14%) of 2.4 represents the relative importance of the addition of OH to the $R-CH{=}C(CH_3)_2$ and $R-CH{=}CH_2$ sites in linalool. The kinetic data suggests that the ratio should be about 1.6 (59%/36%). However, the relatively low yields for the formation of both acetone and glycoaldehyde indicate that conversion of the peroxy radicals to the corresponding alkoxy radicals by reaction with alkyl peroxy or hydro peroxy radicals is relatively low.

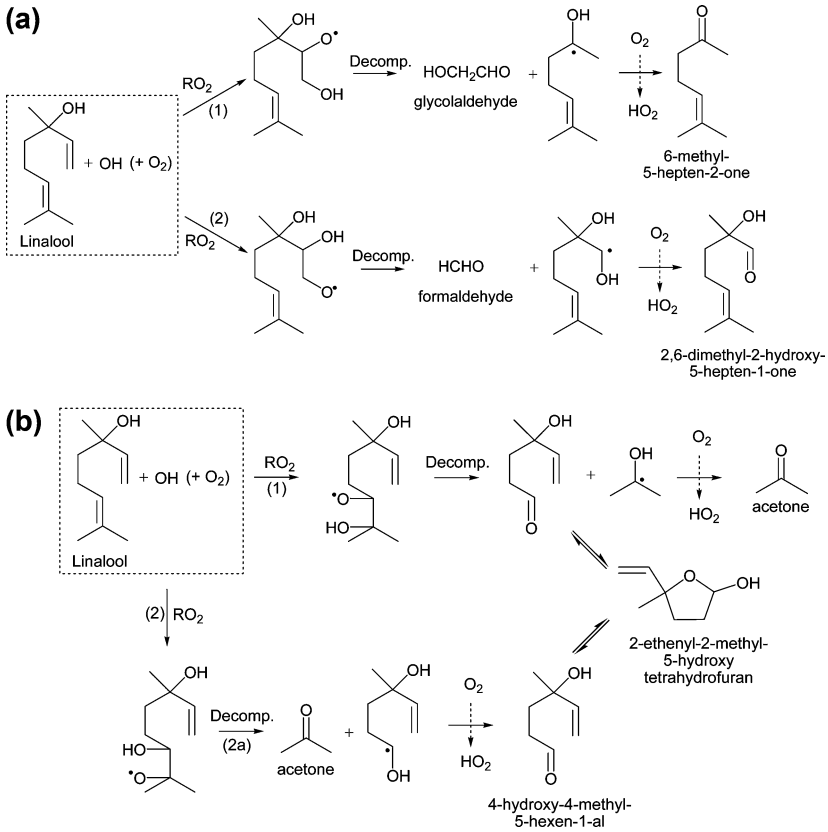

Figure 9. (a) Reaction of linalool with OH (in the absence of NO_X): proposed mechanism scheme for OH attack at the R−CH═CH_2 double bond. (b) Reaction of linalool with OH (in the absence of NO_X): proposed mechanism scheme for OH attack at the R−CH═C$(CH_3)_2$ double bond.

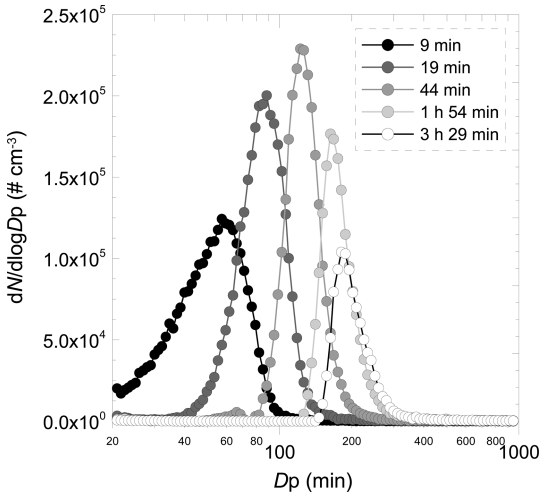

Figure 10. Reaction of linalool with OH (in the absence of NO_X): SOA particle size distribution obtained over the course of the reaction.

Aerosol Formation. The relatively rapid reaction of OH radicals with the unsaturated alcohols means that investigations on SOA formation in these reactions are simplified compared to studies of the corresponding reactions with O_3. The photolyses were carried out using only one lamp in order to reduce the influence of UV light on the SOA formation rate,[51] and to limit the increase of temperature during the reactions, which could have an impact on gas-particle partitioning and the chemical mechanism.[52−54] Under our experimental conditions, SOA formation was observed 5−20 min after photolysis commenced. Figure 10 shows an example of the particle size distribution over the course of the reaction. Growth of the particles by condensation reaches a maximum, and then decreases due to coagulation and wall loss.

The SOA yield from the OH radical-initiated oxidation of 3-methyl-1-penten-3-ol was in the range of 0.8−1.5% under our experimental conditions, while the corresponding reaction of 6-methyl-5-hepten-2-ol led to a SOA formation yield of 0.2−0.8%. Experiments carried out on the oxidation of linalool led to SOA formation yields ranging from 14 to 52%. Thus, formation of SOAs from the oxidation of linalool is considerably more efficient than for the other two unsaturated alcohols investigated. It is of interest to compare the SOA yield of 0.8−1.5% obtained for the oxidation of 3-methyl-1-penten-3-ol to that of ∼0.1% reported for the structurally similar molecule 2-methyl-3-buten-2-ol ($(CH_3)_2C(OH)CH{=}CH_2$).[55] Previous studies on SOA formation from the OH-initiated oxidation of linalool have been carried out in the presence of NO_X, and the reported mass yields were in the range of 4−18%.[18,20,24,25] These yields are considerably lower than found in this work, however, the SOA mass yields obtained from NO_X-free experiments has been found to be significantly higher than in experiments conducted in the presence of NO_X. For example, a NO_X dependence for SOA formation has previously been observed for the OH-initiated reaction of isoprene[56] and α-pinene.[57] It has been suggested that, for low NO_X-conditions, peroxy radicals will react with RO_2 or HO_2 radicals rather than NO, leading to the formation of organic acids with low volatilities, which will increase SOA mass yields.[58]

5. ATMOSPHERIC IMPLICATIONS

The rate coefficients obtained in this study for the reactions of three unsaturated alcohols with ozone and OH radicals can be used to estimate their tropospheric lifetimes with respect to reaction with these oxidants. Using the 24 h average atmospheric concentration of ozone, 7×10^{11} molecules cm^{-3},[59] and the 12 h daytime average concentration of OH radicals, 2×10^{6} molecules cm^{-3},[60] the calculated lifetimes due to reaction with OH radicals are 49 min, 1.4 h, and 2.2 h for linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol, respectively, while those due to reaction with ozone are 58 min, 1.1 h, and 3 days for linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol, respectively. Hence, linalool, 6-methyl-5-hepten-2-ol, and 3-methyl-1-penten-3-ol have relatively short lifetimes and will be degraded close to their emission sources. Long-range transport of these compounds will be of little importance. The atmospheric degradation of unsaturated alcohols by reaction with OH radicals and ozone will lead to the formation of various carbonyl compounds, which may influence the composition of the lower troposphere. Low molecular weight carbonyl compounds such as acetone, formaldehyde, hydroxyacetone, and glycolaldehyde will be degraded by photolysis and reaction with OH radicals with atmospheric lifetimes estimated from a few hours to a few days.[61−64] Acetone has been recognized as a source of HO_X in the upper troposphere and may have an effect on the stratospheric ozone budget.[61] Hydroxyacetone and glycolaldehyde have been detected in both gas and particulate phases in various forest environments, and it is likely that a significant fraction of these compounds might arise through the degradation of BVOCs.[65]

In general, the three unsaturated alcohols investigated in this work are unlikely to make a significant contribution to SOA formation in the atmosphere through reaction with ozone or OH radicals. However, it is possible that the reaction of linalool with OH under low NO_X conditions close to emission sources such as forested areas could constitute a source of condensed organic material that might be rapidly produced due to the high reactivity of linalool. A detailed examination of SOA formation from the OH-initiated oxidation of linalool as a function of NO_X under atmospheric conditions would be of interest.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Data obtained in the absolute measurements of the reaction of ozone with the studied alcohols and the SOA formation yield from the ozone and OH reactions are available. O_3- and OH-initiated gas phase oxidation mechanisms are also included. Plots of the gas phase oxidation products from the ozonolysis reaction of linalool and the SOA mass concentration versus the time from the OH reaction with linalool are showed. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by EUROCHAMP 2, the Labex VOLTAIRE, and the French Program of Atmospheric Chemistry (CHAT-LEFE) of CNRS. We also thank the staff of CEAM for their assistance with the EUPHORE chamber experiments.

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