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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 O₃ and OH Radicals

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6 2 **methyl-1-penten-3-ol with O₃ and OH radicals**
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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 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) determined for the three compounds are: linalool, $k_{\text{O}_3} = (4.1 \pm 1.0) \times 10^{-16}$ and $k_{\text{OH}} = (1.7 \pm 0.3) \times 10^{-10}$; 6-methyl-5-hepten-2-ol, $k_{\text{O}_3} = (3.8 \pm 1.0) \times 10^{-16}$ and $k_{\text{OH}} = (1.0 \pm 0.3) \times 10^{-10}$; 3-methyl-1-penten-3-ol, $k_{\text{O}_3} = (5.2 \pm 0.6) \times 10^{-18}$ and $k_{\text{OH}} = (6.2 \pm 1.8) \times 10^{-11}$. From the kinetic data it is estimated that for the reaction of O_3 with linalool, attack at the $\text{R-CH=C(CH}_3)_2$ group represents around $(93 \pm 52)\%$ ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the overall reaction with reaction at the R-CH=CH_2 group accounting for about $(1.3 \pm 0.5)\%$ ($k_{3\text{-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). In a similar manner it has been calculated that for the reaction of OH radicals with linalool, attack of the OH radical at the $\text{R-CH=C(CH}_3)_2$ group represents around $(59 \pm 18)\%$ ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the total reaction while addition of OH to the R-CH=CH_2 group is estimated to be around $(36 \pm 6)\%$ ($k_{3\text{-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). Analysis of the products from the reaction of O_3 with linalool confirmed that addition to the $\text{R-CH=C(CH}_3)_2$ 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 $[(\text{CH}_3)_2\text{COO}]^*$ 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 SOA 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-pentene-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 SOA were observed in the reactions of OH with linalool although the initial concentrations of

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3 1 reactants were quite high. The importance of linalool in the formation of SOA in the
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6 2 atmosphere requires further investigation. The impact following releases of these unsaturated
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8 3 alcohols into the atmosphere are discussed.
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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 methylbutenols (e.g. 2-methyl-3-buten-2-ol, MBO232) and oxygenated monoterpenes (e.g. linalool). These compounds are highly reactive towards the major atmospheric oxidants: hydroxyl radicals (OH), ozone (O₃), nitrate radicals (NO₃) and chlorine atoms (Cl), leading to very short atmospheric lifetimes (i.e. few hours or less).¹ These oxidation processes have been shown to produce secondary pollutants such as ozone and oxygenates impacting on the tropospheric chemical composition.²⁻⁷ In order to understand and assess the role of unsaturated alcohols and biogenic volatile organic compounds (BVOC) in atmospheric chemistry, it is important not only to quantify their emissions and atmospheric abundance but also to 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) ((CH₃)₂C=CHCH₂CH₂C(OH)(CH₃)CH=CH₂), 6-methyl-5-hepten-2-ol ((CH₃)₂C=CHCH₂CH₂CH(OH)CH₃) and 3-methyl-1-penten-3-ol (CH₂=CHC(OH)(CH₃)CH₂CH₃). It has been reported that linalool is emitted from vegetation, especially from needles of conifer *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 ((CH₃)₂C=CHCH₂CH₂CH(OH)CH₃) and 3-methyl-1-penten-3-ol

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3 1 $(\text{CH}_2=\text{CHC}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3)$ may also be important, since these molecules have
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6 2 structural features in common with linalool $((\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}=\text{CH}_2)$.
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8 3 Hence, the mechanisms for their oxidation could be useful in elucidating the reaction
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10 4 pathways for the OH and O_3 initiated oxidation of linalool.
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12 5 However, no data on the oxidation of 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol
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14 6 have been reported, and a limited number of kinetic, product distribution and aerosol
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16 7 formation studies on the reactions of OH and O_3 with linalool have previously been
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18 8 reported.^{2,3,16-26} To our knowledge, for the OH reaction, no experiment has been conducted in
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20 9 the absence of NO_x . The present paper reports kinetic and product studies on the reactions of
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22 10 O_3 and OH radicals (NO_x -free conditions) with linalool, 6-methyl-5-hepten-2-ol and 3-
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24 11 methyl-1-penten-3-ol. In addition, the yields of aerosol formation from these reactions have
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26 12 also been determined in this work.
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34 14 **2. Experimental methods**

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36 15 The experiments have been performed using three atmospheric simulation chambers: the
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38 16 EUPHORE facility (CEAM-Valencia, Spain) and two different chambers (7300 L and 200 L)
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40 17 at ICARE (CNRS-Orléans, France). The rate coefficients for the reactions of O_3 with the three
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42 18 compounds together with the rate coefficients for the reactions of OH with 3-methyl-1-
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44 19 penten-3-ol and 6-methyl-5-hepten-2-ol were measured using the ICARE 7300 L chamber,
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46 20 while the 200 L chamber was employed for the kinetic study of OH with linalool. The
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48 21 mechanistic study of the O_3 -initiated oxidation of 6-methyl-5-hepten-2-ol was conducted at
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50 22 EUPHORE, while the O_3 - and OH-initiated oxidation of linalool and 3-methyl-1-penten-3-ol
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52 23 were performed using the 7300 L ICARE chamber.
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3 1 **7300L ICARE chamber.** Experiments were carried out at room temperature and 760 Torr of
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5 2 purified air (< 5% relative humidity). The chamber, made of Teflon foil, has been previously
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7 3 described elsewhere.²⁷ It is covered by a black opaque curtain in order to work in the dark for
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9 4 ozone reaction studies and is equipped with 14 lamps with a wavelength of 254 nm in order to
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11 5 perform OH-initiated reaction experiments (UV-A T-40 L, 40W, Viber Lourmat). Rapid
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13 6 mixing of reactants was ensured with two fans made of Teflon during all the experimental
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15 7 runs. After each experiment, the chamber was flushed with purified air (flow of around 100 L
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17 8 min⁻¹) in order to purge the remaining chemicals from the system. For the introduction of
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19 9 compounds in the liquid state at room temperature, a known volume of reactant was
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21 10 introduced into an impinger (gently heated when necessary) and further driven into the
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23 11 chamber by a stream of purified air. Gaseous compounds were introduced using a calibrated
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25 12 cylinder (0.9 L) connected to two pressure sensors (0-10 Torr and 0-100 Torr, MKS Baratron).
26
27 13 Reactants were monitored using an *in situ* Fourier Transform Infra Red spectrometer (FT-IR,
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29 14 Nicolet 5700 Magna), coupled to a White-type mirror system (optical paths: 129 and 148 m).
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31 15 The instrument is operated in the mid-IR region (4000 to 650 cm⁻¹). Spectra have been
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33 16 recorded by co-adding 130 interferograms within 5 minutes at a resolution 1 cm⁻¹. The
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35 17 alcohols and reference compounds concentrations were determined using calibrated reference
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37 18 spectra. Temperature and relative humidity data are recorded by a combined sensor. Ozone
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39 19 was generated using an electric discharge on a flow of oxygen (O₂, Air liquide), which was
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41 20 capable of a rapid introduction of ozone into the chamber. Ozone concentration was
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43 21 continuously measured by a monitor (Thermo Environment 49C or Horiba APOA-360) based
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45 22 on its ultraviolet absorption at 254 nm. A measurement point was obtained at least every 10
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47 23 seconds. Secondary Organic Aerosols (SOA), formed in the reactions of ozone and OH
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49 24 radicals with the unsaturated alcohols, were also monitored over the course of the reactions
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51 25 using a scanning mobility particle sizer (SMPS, Model TSI 3080). The SMPS consists of a
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3 1 Differential Mobility Analyser (DMA, Model TSI 3081) and Condensation Nuclei Counter
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5 2 (CNC, Model TSI 3022). The sample flow was fixed at 0.2 L min^{-1} , and the size distribution
6
7 3 of the particles formed was monitored during all the experiments. The particle size diameter
8
9 4 ranged from 20 to 1000 nm and was acquired every 5 minutes. Measurements started around
10
11 5 one hour before each experiment in order to characterize particle background in the chamber.
12
13 6 Statistical correction for multiple charges was applied to the measured size distribution. The
14
15 7 density of particles was assumed to be 1 g cm^{-3} .
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18 8 **200L ICARE chamber.** The 200 L FEP Teflon chamber was surrounded by six lamps
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20 9 (Sylvania, G30W) with irradiation centred at 254 nm. The chamber was suspended in a
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22 10 wooden box with internal faces covered by aluminium foil. Reactants were introduced into
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24 11 the Teflon bag by streaming purified air through a calibrated bulb (579 mL). Hydrogen
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26 12 peroxide was used as the source of OH radicals, and introduced by liquid injection into a
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28 13 stream of purified air flowing directly into the chamber. A Gas Chromatograph, coupled to a
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30 14 Flame Ionisation Detector (GC-FID, Star 3600 CX, Varian), was used to determine the
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32 15 concentration of reactants in the chamber. Chromatographic separations were performed with
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34 16 a DB-1 capillary column (J&W Scientific, 30 m, 0.32 mm, $5 \mu\text{m}$ film) operated at various
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36 17 temperatures from 353 K to 508 K.
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38
39 18 **EUPHORE Chamber.** Gas phase product investigations of the ozonolysis of 6-methyl-5-
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41 19 hepten-2-ol were performed at the EUropean PHOtoREactor (EUPHORE), the large outdoor
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43 20 simulation chamber in Valencia, Spain. A detailed description of the EUPHORE facility can
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45 21 be found elsewhere.²⁸⁻³¹ It consists of an approximately 200 m^3 hemispherical chamber made
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47 22 of FEP Teflon. Two fans are interfaced into the chamber which ensure homogeneous mixing
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49 23 of the air. The chamber is equipped with an *in situ* FT-IR spectrometer (Magna 550) coupled
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51 24 to a White-type mirror system with an optical path of 553.5 m. Infra-red spectra were
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53 25 recorded every 5 minutes co-adding 280 spectra with a resolution of 1 cm^{-1} . The reactant and
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1 gas phase products were also monitored by gas chromatography using several different
2 detectors (photo-ionisation detector (PID), electron capture detector (ECD) and mass
3 spectrometer detector (SM)). Carbonyl compounds were sampled on DNPH-cartridges and
4 the derivatives were analysed by HPLC-UV. Ozone was measured using a monitor employing
5 UV absorption. Particle formation was monitored by a scanning mobility particle sizer (SMPS)
6 and a tapered elemental oscillating microbalance (TEOM).

7
8 While the OH reaction rate coefficients have been determined only by the relative rate method,
9 those for the reactions of ozone were measured using both relative and absolute rate methods.
10 In a conventional relative rate method, the values of the rate coefficients are determined by
11 following the parallel decays of the alcohols and the organic reference compounds. Loss of
12 the alcohols and the reference compounds occur in the following reactions:



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

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

22 where $[\text{Alcohol}]_0$, $[\text{Ref}]_0$, $[\text{Alcohol}]_t$ and $[\text{Ref}]_t$ are the concentrations (in molecule cm^{-3}) of
23 the unsaturated alcohol and the reference organic compound at times t_0 and t , respectively.
24 k_{Alcohol} and k_{ref} are the rate coefficients for the reactions of OH radicals or ozone with the
25 unsaturated alcohol and reference compound, respectively. To take into account decay of

1 substrate and reference compounds due to dilution and wall loss (no photolysis of these
2 compounds was observed under our experimental conditions), the terms $k_L(\text{Alcohol})$ and
3 $k_L(\text{Ref})$ are introduced into the equation. These terms were determined from the pseudo-first
4 order decay of the alcohol and reference compounds in the absence of any oxidants. The
5 quoted error attributed to the determined rate coefficient k_{Alcohol} results from one-standard
6 deviation (1σ) from the slope of the plot of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_L(\text{Alcohol})\times t$ against
7 $\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_L(\text{Ref})\times t$ and the uncertainty in the rate coefficient of the reference
8 compound. Butyl vinyl ether, isoprene, cyclohexene, 3-methyl-3-buten-1-ol and propene were
9 selected as reference organic compounds. In the study using the 7300 L chamber, the
10 reference compounds were monitored by FT-IR spectroscopy over the following wavenumber
11 ranges: cyclohexene, 3054-3013 cm^{-1} ; propene, 966-872 cm^{-1} ; butyl vinyl ether, 1239-1168
12 cm^{-1} ; 3-methyl-3-buten-1-ol, 3118-3055 cm^{-1} .

13
14 In the absolute kinetic studies of the reactions of ozone with unsaturated alcohols, the
15 concentrations of alcohols were in excess over those of ozone, typically $[\text{Alcohol}]_0 = (1.35 -$
16 $12.8) \times 10^{13}$ and $[\text{Ozone}]_0 = (0.69 - 13.9) \times 10^{12}$ (in molecule cm^{-3}). Under pseudo-first order
17 conditions, ozone decay follows the following kinetic law:

$$18 \quad [\text{O}_3]_t = [\text{O}_3]_0 e^{-k't} \quad \text{where} \quad k' = k [\text{Alcohol}]_0 + k'_0$$

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

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5 2 Production of aerosols was observed from the reaction of unsaturated alcohols with
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8 3 both ozone and OH radicals. Experiments were carried out at room temperature and a relative
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10 4 humidity < 5%. SOA mass yields were estimated from the particle volumetric yields
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12 5 assuming an aerosol density of 1 g cm⁻³. The residual particle concentration prior to the start
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14 6 of the reactions was also measured ($N < 50 \text{ cm}^{-3}$ and $M_0 < 0.1 \mu\text{g m}^{-3}$). After nucleation, the
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16 7 particle number slowly decreased through coagulation or/and wall loss on the Teflon film
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18 8 chamber wall. Particle volume concentration increased over the course of the reaction and
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20 9 decreased due to wall losses at the end of the reaction. Concentration-time profiles of the
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22 10 aerosols were corrected for wall loss using the measured aerosol decay rates at the end of the
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24 11 reaction. SOA mass yields (Y) has been estimated from the formed aerosol mass
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26 12 concentration (M_0 in $\mu\text{g m}^{-3}$) and the consumed concentration of VOCs ($\Delta[\text{Alcohol}]$ in $\mu\text{g m}^{-3}$)
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28 13 ratio:

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

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38 15 The quoted error on the SOA mass yields originates from the uncertainties of the values of M_0
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40 16 and $\Delta[\text{Alcohol}]$, estimated to one-standard deviation (1σ).
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45 18 3. Chemicals

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47 19 The commercial source of chemicals used in this work and their stated purities are as follows:
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49 20 linalool (Acros Organics and Alfa Aesar, 97%), 6-methyl-5-hepten-2-ol (98%, Alfa Aesar), 3-
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51 21 methyl-1-penten-3-ol (98%, Alfa Aesar), propene (99.5%, Air Liquide), cyclohexene (\geq
52
53 22 99.5%, Fluka), butyl vinyl ether (98%, Sigma Aldrich), 3-methyl-3-buten-1-ol (97%, Sigma
54
55 23 Aldrich), propyl vinyl ether (99%, Sigma Aldrich), hydrogen peroxide solution (50% in water,
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3 1 Sigma Aldrich), cyclohexane ($\geq 99.5\%$, Sigma Aldrich) and di-*n*-butylether ($\geq 99\%$, Sigma
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6 2 Aldrich).

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10 4 **4. Results and discussion**

13 5 **4.1 Reaction with ozone**

15 6 **Kinetic measurements.** Examples of pseudo-first order decays of ozone as a function of
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17 7 reaction time for different concentrations of linalool are given in Figure 1. The reaction rate
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19 8 coefficients were derived from the least square data fits of plots of $(k'-k'_0)$ against
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21 9 $([\text{Alcohol}]_0)$. Figures 2(a-c) display plots of $(k'-k'_0)$ versus the alcohol concentrations for the
22
23 10 reactions of ozone with linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol,
24
25 11 respectively. To avoid any complications due to the generation of OH radicals in the chemical
26
27 12 system, most runs were conducted in the presence of an OH scavenger: cyclohexane ($7.8 \times$
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29 13 10^{15} molecule cm^{-3}) for 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol, and di-*n*-
30
31 14 butylether ($(1.2 - 2.4) \times 10^{15}$ molecule cm^{-3}) for linalool. The rate coefficients for the
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33 15 reactions of cyclohexane and di-*n*-butylether with OH radicals are $k = (6.97 \pm 1.39) \times 10^{-12}$
34
35 16 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,³² and $k = (2.80 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,¹ at 298 K, respectively.
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37 17 During the absolute rate method experiments, the ozone monitor initially showed slight
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39 18 negative interferences in the presence of linalool and 6-methyl-5-hepten-2-ol. In these
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41 19 experiments, injection of ozone was performed when the ozone monitor signal was stable,
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43 20 typically 15 minutes after the introduction of the alcohol. Due to the low vapour pressure of
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45 21 unsaturated alcohols, ozone was introduced after the compound. Therefore, the ozone leakage
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47 22 first order rate coefficient was determined in a series of separate experiments. The average
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49 23 rate coefficient for ozone loss was $k_0 = (2.5 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$. The rate coefficients (in cm^3
50
51 24 $\text{molecule}^{-1} \text{ s}^{-1}$) obtained for the reactions of O_3 with the three alcohols at $296 \pm 3 \text{ K}$ in 760
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53 25 Torr of purified air are as follows:



4 Additional experiments have been performed using the relative rate method. Propene was
5 used as the reference for the reaction of 3-methyl-1-penten-3-ol with ozone, and butyl vinyl
6 ether and propyl vinyl ether for the ozonolysis of linalool and 6-methyl-5-hepten-2-ol.
7 Cyclohexane was added to the gas mixtures in sufficient concentration to scavenge more than
8 90% of the OH radicals potentially formed through the ozonolysis reactions. Preliminary
9 experiments were carried out to determine the loss of the three unsaturated alcohols and
10 organic references in the absence of ozone. Compounds and references were introduced into
11 the chamber and their temporal behaviours were observed from 30 minutes to one hour in
12 order to assess their respective total loss rate coefficients via dilution and wall loss. Initial
13 concentrations were (in 10¹³ molecule cm⁻³): [Alcohol]₀ = 1.1 - 7.5 and [Reference]₀ = 1.1 -
14 5.8. Kinetic measurements commenced after the addition of ozone, and the parallel decays of
15 the substrates and references were monitored and quantified using FT-IR spectroscopy. The
16 duration of the runs ranged from 10 to 30 minutes for linalool and 6-methyl-5-hepten-2-ol and
17 from 20 minutes to one hour for 3-methyl-1-penten-3-ol. Plots of $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) -$
18 $k_L(\text{Alcohol}) \times t$ 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
19 shown in Figures 3(a-c). The initial conditions and results are listed in the Table 1. Rate
20 coefficients have been calculated using the following values for the reference compounds (in
21 cm³ molecule⁻¹ s⁻¹): $k(\text{propene} + \text{O}_3) = (1.0 \pm 0.1) \times 10^{-17}$,³³ $k(\text{propyl vinyl ether} + \text{O}_3) = (2.4 \pm$
22 $0.4) \times 10^{-16}$ and $k(\text{butyl vinyl ether} + \text{O}_3) = (2.9 \pm 0.2) \times 10^{-16}$.³⁴ The rate coefficients
23 determined (in cm³ molecule⁻¹ s⁻¹) for the three unsaturated alcohols are:





6 2 These rate coefficients values are in good agreement with those derived from the absolute rate
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8 3 technique. Therefore, we recommend the average values of the rate coefficients obtained from
9
10 4 both relative and absolute rate studies (in cm³ molecule⁻¹ s⁻¹):
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23 9 No kinetic data have been reported for the reactions of O₃ with 6-methyl-5-hepten-2-ol and 3-
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25 10 methyl-1-penten-3-ol, while two previous investigations on the reaction with linalool have
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27 11 been carried out.^{16,19} The rate coefficient determined by Atkinson et al.¹⁶ was obtained using
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29 12 the relative rate method, with 2-methyl-2-butene used as the reference compound. Taking $k(2$ -
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31 13 methyl-2-butene + O₃) = 4.1×10^{-16} cm³ molecule⁻¹ s⁻¹,³³ a value of the rate coefficient for the
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33 14 reaction of O₃ with linalool of $k = (4.5 \pm 0.1) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ was derived, which is
34
35 15 in very good agreement with our value of ($k = (4.1 \pm 1.0) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹). Grosjean
36
37 16 and Grosjean¹⁹ employed an absolute rate technique to study the reaction in which the
38
39 17 concentration of linalool was in large excess over ozone. The authors could only report an
40
41 18 upper limit for the rate coefficient of $k \geq (3.15 \pm 0.23) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹, since the
42
43 19 rate of ozone decay in the system was similar to the response time of the ozone monitor.
44
45
46
47
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49 20 The data obtained in the present work indicate that the rate coefficients for the reactions of
50
51 21 ozone with linalool and 6-methyl-5-hepten-2-ol are similar, while that for reaction with 3-
52
53 22 methyl-1-penten-3-ol is around two orders of magnitude lower. The high reactivity of linalool
54
55 23 and 6-methyl-5-hepten-2-ol can be explained, at least in part, by the high degree of
56
57 24 substitution of the double bond (–CH=C(CH₃)₂) at which the reaction with ozone is expected
58
59 25 to proceed. As expected, the low degree of substitution of the double bond (–CH=CH₂) leads
60

1 to the observed reduction in reactivity of 3-methyl-1-penten-3-ol towards O₃, which is in
2 agreement for the corresponding reaction with the structurally similar compound 2-methyl-3-
3 buten-3-ol (CH₂=CHC(CH₃)₂(OH)) within the stated uncertainties ($k = (1.0 \pm 0.6) \times 10^{-17} \text{ cm}^3$
4 molecule⁻¹ s⁻¹).³³

5 It is of interest to note that the value of the rate coefficient for the reaction of O₃ with linalool
6 is close to the sum of the rate coefficients for the reactions of O₃ with the other two
7 unsaturated alcohols investigated:

$$k(6\text{-methyl-5-hepten-2-ol} + \text{O}_3) + k(3\text{-methyl-1-penten-3-ol} + \text{O}_3) \approx k(\text{linalool} + \text{O}_3)$$

8 The rate coefficients obtained in this work suggest that for the reaction of O₃ with linalool,
9 attack at the R-CH=C(CH₃)₂ group represents around (93 ± 52)% ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of
10 the overall reaction with reaction at the R-CH=CH₂ group accounting for about (1.3 ± 0.5)%
11 ($k_{3\text{-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). Atkinson et al.¹⁶ and Shu et al.³ previously proposed that 97% of
12 the reaction with ozone proceeds by addition to the R-CH=C(CH₃)₂ group and only 3% to the
13 R-CH=CH₂ group in agreement with the estimates from the present study.

14
15
16 **Gas phase product studies.** For each unsaturated alcohol, a set of three experiments was
17 performed in the presence of cyclohexane as a scavenger for OH radicals. In all the
18 experiments, the alcohol was injected first into the chamber followed by the addition of
19 cyclohexane. Prior to the addition of ozone, the organic compounds were monitored for at
20 least 30 minutes. The reactant concentrations employed were in the range (1.62 - 4.49) × 10¹³
21 molecule cm⁻³ at ICARE and (4.91 - 5.59) × 10¹² molecule cm⁻³ at EUPHORE. Figure 4
22 displays IR spectra obtained from the ozonolysis of linalool at different stages of the reaction.
23 The reference spectrum of linalool is shown in panel A, while panels B and C show the IR
24 spectra of linalool and O₃ at the start of the reaction and after 2 hours of reaction respectively.
25 Panels D, E, F and G display the IR reference spectra of acetone, formaldehyde,

1 hydroxyacetone and formic acid, respectively. A typical residual IR spectrum (after
2 subtraction of the reactants and all identified products) is shown in panel H. The derived
3 product formation yields for the reactions of ozone with the unsaturated alcohols are
4 summarized in Tables 2 (a-c).

5 Products identified from the reaction of ozone with linalool were acetone ($35 \pm 6\%$),
6 formaldehyde ($32 \pm 6\%$) and hydroxyacetone ($28 \pm 5\%$). Ozonolysis of 3-methyl-1-penten-3-
7 ol gave formaldehyde and 2-butanone as the major products with formation yields of ($29 \pm$
8 4%) and ($46 \pm 3\%$), respectively. A stoichiometric ratio of $\Delta[\text{O}_3]/\Delta[3\text{-methyl-1-penten-3-ol}] =$
9 1.1 ± 0.1 was obtained in the absence of cyclohexane suggesting that the formation yield of
10 OH radicals in the system was negligible. The products identified and quantified from the
11 reaction of ozone with 6-methyl-5-hepten-2-ol were: acetone ($31 \pm 7\%$), formaldehyde ($40 \pm$
12 10%), hydroxyacetone ($17 \pm 2\%$), formic acid ($16 \pm 4\%$) and methylglyoxal ($10 \pm 1\%$).
13 Formation of 4-hydroxypentanal as a product of the ozonolysis was also expected, however, a
14 sample of this compound was not commercially available and hence it could not be positively
15 quantified. The yield of 4-hydroxypentanal was tentatively quantified using 4-pentanal as a
16 surrogate, which was introduced into the gas mixture at the end of the experiment. A yield of
17 4-hydroxypentanal of around 34% was estimated using HPLC-UV, assuming the response
18 factor for the DNPH derivatives of both 4-pentanal and 4-hydroxypentanal were the same. In
19 addition, cyclohexanone and cyclohexanol have also been identified as products by GC-MS,
20 indicating the formation of OH radicals in the ozonolysis reaction.³⁵ Then, OH formation
21 yield from the ozonolysis of 6-methyl-5-hepten-2-ol has been derived and found to be ($65 \pm$
22 20%) which is similar to that of linalool ($66 \pm 10\%$).²²

23 To date, of the unsaturated alcohols studied in this work, only the gas phase products from the
24 ozonolysis of linalool have been reported.^{2,3,23} Grosjean and Grosjean² performed experiments
25 with a relative humidity of 50%, while the other studies were conducted with relative

1 humidities below 10%. The acetone yield (35 ± 6)% obtained in this work agrees with that
2 reported by Grosjean and Grosjean² (28 ± 1)% but is higher than that from Shu et al.³ ($21.1 \pm$
3 2.4)% and Lee et al.²³ (16 ± 1)%. The measured yield of formaldehyde (32 ± 6)% is in line
4 with the previously reported values by Shu et al.³ (36 ± 6)% and Lee et al.²³ (34 ± 3)%.
5 Hydroxyacetone was detected as a product of the ozonolysis of linalool in this work with a
6 yield of (28 ± 5)%. This product has not previously been observed, however, Grosjean and
7 Grosjean² detected methylglyoxal as a reaction product with a yield of (11 ± 1)% following
8 derivatization with DNHP. This product could not be resolved under our experimental
9 conditions, however as mentioned by Grosjean and Grosjean,² the reaction of hydroxyacetone
10 and methylglyoxal with DNHP leads to the same derivative. Hence, it is possible that
11 hydroxyacetone may interfere in the quantification of methylglyoxal. 4-Hydroxy-4-methyl-5-
12 hexen-1-al (or 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran) has also been reported as a
13 major product from the ozonolysis of linalool with a formation yield of (85 ± 14)%,³ and (50
14 ± 9)%,²³ 5-Ethenyldihydro-5-methyl-2(3*H*)-furanone and acetaldehyde were also detected as
15 products with yields of (12.6 ± 2.5)%,³ and (14 ± 1)%,²³ respectively.

16
17 It is well established that the reaction of ozone with unsaturated alcohols proceeds by
18 electrophilic addition of ozone to the double bond.³⁶ This leads to a primary ozonide, which
19 decomposes to an energy-rich Criegee biradical and the corresponding carbonyl compound. A
20 mechanistic scheme for the reaction of ozone with 3-methyl-1-penten-3-ol is shown in Figure
21 5 based on the observed and/or expected products. This reaction proceeds by initial addition
22 of ozone to the R-CH=CH₂ group forming an ozonide, which then rapidly decomposes to
23 either C₂H₅C(OH)(CH₃)CHO (3-hydroxy-3-methyl-1-butanal) plus the [CH₂OO]* biradical
24 or HCHO plus the [C₂H₅C(OH)(CH₃)CHOO]* biradical. The energy-rich [CH₂OO]* biradical,
25 can be either stabilized or decomposes to form HCOOH, CO, CO₂, H₂O, H₂ and the OH

1 radical.^{37,38} The Criegee intermediate $[\text{C}_2\text{H}_5\text{C}(\text{OH})(\text{CH}_3)\text{CHOO}]^*$, formed through channel
2 (2), can also be either stabilized to form 3-hydroxy-3-methyl-1-butanal (channel (2a)), or
3 decomposes to form CO_2 and the $\text{C}_2\text{H}_5\text{C}(\text{OH})(\text{CH}_3)$ alkoxy radical. This radical will rapidly
4 react with O_2 to form 2-butanone. Based on the observed yield of 2-butanone, the proposed
5 mechanism suggests that channel (2) accounts for at least 46% of the reaction of O_3 with 3-
6 methyl-1-penten-3-ol. Thus, it appears that decomposition of the primary ozonide in channels
7 (1) and (2) is of equivalent importance. The mechanism suggests that the yield of
8 formaldehyde should at least be the same as that for 2-butanone. However, the formaldehyde
9 formation yield was found to be only 29%, which indicates that either formaldehyde is
10 removed from the system in secondary processes or there is an additional source of 2-
11 butanone not identified in this work.

12 The available kinetic data suggest that the reactions of ozone with linalool and 6-methyl-5-
13 hepten-2-ol occur mainly at the $\text{R-CH}=\text{C}(\text{CH}_3)_2$ double bond, and that addition at the R-
14 $\text{CH}=\text{CH}_2$ double bond will only represent a minor pathway. Decomposition of primary
15 ozonides can lead either to the formation of acetone and the corresponding Criegee biradical
16 (CI_1) in channel 1, or form the biradical $[(\text{CH}_3)_2\text{COO}]^*$ (CI_2) and the carbonyl compounds 4-
17 hydroxy-4-methyl-5-hexen-1-al and 4-hydroxypentanal from linalool and 6-methyl-5-hepten-
18 2-ol, respectively. Moreover, the observed products (formaldehyde and hydroxyacetone) and
19 the OH formation yields from the ozonolysis of linalool and 6-methyl-5-hepten-2-ol indicate
20 that hydroperoxide channel is an important pathway in the fate of $[(\text{CH}_3)_2\text{COO}]^*$ via the
21 formation of the $[\text{CH}_3\text{C}(\text{OOH})=\text{CH}_2]^*$ isomer.^{39,40}

22
23 **Aerosol formation.** Under our experimental conditions, the SOA mass yields from the
24 ozonolysis of 3-methyl-1-penten-3-ol ranged from 0 to 1.9% in the absence of OH scavenger
25 and from 0.08 to 0.3% in the presence of cyclohexane. The ozonolysis of 6-methyl-5-hepten-

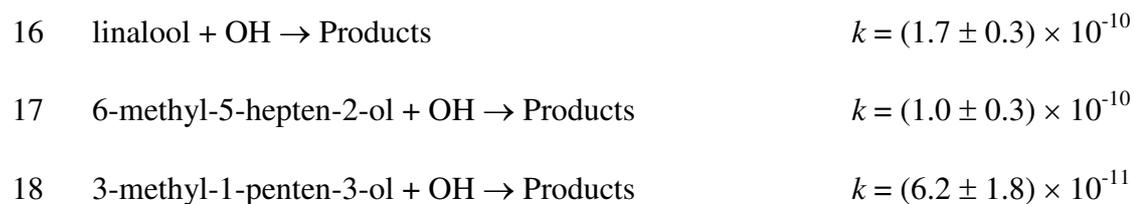
1
2
3 1 2-ol led to a SOA mass yield of around 2% in the absence of OH scavenger and 0.5% in the
4
5
6 2 presence of cyclohexane. Linalool ozonolysis experiments showed that for reactions
7
8 3 performed in the presence of cyclohexane, the SOA mass yields varied from 1.4% to 1.9%,
9
10 4 while in the absence of an OH scavenger the SOA yield was approximately 10%. The SOA
11
12 5 yields from the ozonolysis of linalool in the presence of an OH scavenger obtained in this
13
14
15 6 study are in broad agreement with that of 1% reported by Lee et al.²³ In the absence of a
16
17 7 scavenger, the 10% SOA yield determined in this work is in reasonable agreement with the
18
19 8 value of 8% reported by Hoffmann et al.¹⁸, although considerably higher than the estimate of
20
21 9 2% obtained by Chen et al.²⁶ The present results show that SOA formation from the
22
23 10 ozonolysis of the unsaturated alcohols studied is relatively low. Nevertheless, in the absence
24
25 11 of OH scavengers the SOA mass yield is higher than in their presence, which is in agreement
26
27 12 with previous observations from studies on the ozonolysis of alkenes.⁴¹⁻⁴³
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34 14 **4.2 Reaction with OH radicals**

35
36 15 ***Kinetic measurements.*** OH radicals were generated through the photolysis of H₂O₂ at 254 nm.
37
38 16 Preliminary experiments were performed in order to check the stability of the alcohols in the
39
40 17 presence of the reference compounds and H₂O₂ in the dark. Additional tests were carried out
41
42 18 in order to check the photostability of the organic compounds in the absence of H₂O₂. The
43
44 19 duration of the tests ranged from 30 minutes to more than one hour. The results of these
45
46 20 experiments showed that decay of the organic compounds in the absence of H₂O₂ was
47
48 21 negligible except for loss at the wall and by dilution. No loss other than the reaction with OH
49
50 22 radicals has been observed for linalool and the reference compounds. The experiments on 3-
51
52 23 methyl-1-penten-3-ol and 6-methyl-5-hepten-2-ol were conducted in the 7300 L chamber
53
54 24 using FT-IR as the analytical tool, while the study of the reaction of linalool with OH was
55
56 25 performed in the 200L chamber using GC-FID for monitoring the decays of the organic
57
58
59
60

1 compounds. The initial concentrations used in the 7300 L chamber were: $[\text{Alcohol}]_0 = (2.6 -$
 2 $4.8) \times 10^{13}$; $[\text{Reference}]_0 = (2.6 - 5.3) \times 10^{13}$; $[\text{H}_2\text{O}_2]_0 = (3 - 4) \times 10^{14}$ molecule cm^{-3} . The
 3 initial concentrations of reactants employed in the 200 L chamber for the linalool experiments
 4 were (in molecule cm^{-3}): $[\text{Linalool}]_0 = (2.0 - 6.6) \times 10^{14}$; $[\text{Reference}]_0 = (2.5 - 6.6) \times 10^{14}$;
 5 $[\text{H}_2\text{O}_2]_0 = (1 - 4) \times 10^{15}$. Experimental durations varied from 90 to 120 minutes. Plots of
 6 $\ln([\text{Alcohol}]_0/[\text{Alcohol}]_t) - k_L(\text{Alcohol})\times t$ against $(\ln([\text{Ref}]_0/[\text{Ref}]_t) - k_L(\text{Ref})\times t)$ gave good
 7 straight lines, Figures 6(a-c) for linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol
 8 respectively, and the slopes provide values of the rate coefficient ratios $k_{\text{Alcohol}}/k_{\text{Ref}}$. The
 9 reference rate coefficients used to derive the rate coefficients for the reactions of OH with the
 10 three unsaturated alcohols were (in cm^3 molecule $^{-1}$ s $^{-1}$): butyl vinyl ether and propyl vinyl
 11 ether $((1.1 \pm 0.1) \times 10^{-10},^{44})$; isoprene $((1.0 \pm 0.1) \times 10^{-10},^{33})$; propene $((2.9 \pm 0.3) \times 10^{-11},^{33})$;
 12 cyclohexene $(6.8 \pm 1.7) \times 10^{-11},^{36})$ and 3-methyl-3-buten-1-ol $((9.4 \pm 0.4) \times 10^{-10},^{45})$.

13 The experimental conditions and the values obtained for $k_{\text{Alcohol}}/k_{\text{Ref}}$ are listed in Table 3. The
 14 rate coefficients for the studied reactions are taken as the average of different measurements
 15 leading to (at 296 ± 4 K, 760 Torr of purified air, and in cm^3 molecule $^{-1}$ s $^{-1}$):



19 The quoted errors were estimated from the least squares analysis of the relative rate data. In
 20 addition, two runs were conducted in the 7300 L chamber (using FT-IR for analysis) to
 21 measure the decay rate of linalool relative to that of 6-methyl-5-hepten-2-ol for reaction with
 22 OH radicals. The experimental result was $k(\text{linalool} + \text{OH})/k(6\text{-methyl-5-hepten-2-ol}) = 1.4 \pm$
 23 0.2 , which is in reasonable agreement with the rate coefficient ratios determined in
 24 independent measurements (1.7 ± 0.8) .

25

1
2
3 1 In this work, we report the first measurements of the rate coefficients for reaction of OH with
4
5 2 3-methyl-1-penten-3-ol and 6-methyl-5-hepten-2-ol. To our knowledge, this work is the third
6
7 3 determination of the rate coefficient of the reaction of linalool with OH radicals.^{16,21} The rate
8
9 4 coefficient reported for the reaction of OH with linalool by Atkinson et al.¹⁶ was performed
10
11 5 using a relative rate method with isoprene as the reference compound. Based on the IUPAC
12
13 6 recommendation³³ for $k(\text{OH} + \text{isoprene}) = (1.0 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a value of
14
15 7 $k(\text{linalool} + \text{OH}) = (1.57 \pm 0.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived from the rate data in
16
17 8 reasonable agreement with the value determined in this study. The measurement of Bernhard
18
19 9 and Simonich²¹ was also obtained using the relative rate method with styrene as the reference
20
21 10 compound. Taking $k(\text{OH} + \text{styrene}) = (5.8 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁴² leads to a value
22
23 11 $k(\text{linalool} + \text{OH}) = (2.15 \pm 0.58) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is within the stated
24
25 12 uncertainties of the rate coefficient determined in this work.

26
27 13 The rate coefficients determined for the reaction of OH with 3-methyl-1-penten-3-ol ($k = (6.2$
28
29 14 $\pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is around two times higher than that estimated by the SAR
30
31 15 method ($k = 2.95 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).^{47,48} However, it is in line with the reported rate
32
33 16 coefficient for the reaction of OH with the structurally similar compound 2-methyl-3-buten-3-
34
35 17 ol ($\text{CH}_2=\text{CHC}(\text{CH}_3)_2(\text{OH})$) ($k = 6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.³³ The measured rate
36
37 18 coefficient for the OH reaction with 6-methyl-5-hepten-2-ol ($k = (1.0 \pm 0.3) \times 10^{-10} \text{ cm}^3$
38
39 19 $\text{molecule}^{-1} \text{ s}^{-1}$) is very close that calculated from the SAR method ($k = 9.89 \times 10^{-11} \text{ cm}^3$
40
41 20 $\text{molecule}^{-1} \text{ s}^{-1}$).

42
43 21 The kinetic data reported in this work show that (within the stated uncertainties):

44
45 22
$$k(6\text{-methyl-5-hepten-2-ol} + \text{OH}) + k(3\text{-methyl-1-penten-3-ol} + \text{OH}) \approx k(\text{linalool} + \text{OH})$$

46
47 23 in a similar manner to that found for the O₃ kinetic studies.

48
49 24 The reactions of the unsaturated alcohols with OH radicals proceed mainly by addition to the
50
51 25 >C=C< double bond system. The kinetic data indicate that the sum of the rate coefficients for

1 reaction of OH with 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol are close to that for
2 reaction with linalool. Hence, the double bond in each of these molecules exhibits virtually
3 the same reactivity in linalool as they have in the individual molecules. Thus, it is possible to
4 calculate that for the reaction of OH radicals with linalool, attack of the OH radical at the R-
5 $\text{CH}=\text{C}(\text{CH}_3)_2$ group represents around $(59 \pm 18)\%$ ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{\text{linalool}}$) of the total
6 reaction while addition of OH to the R- $\text{CH}=\text{CH}_2$ group is estimated to be around $(36 \pm 6)\%$
7 ($k_{3\text{-methyl-1-penten-3-ol}}/k_{\text{linalool}}$). Calculations using the SAR method^{47,48} suggest that OH addition at
8 the R- $\text{CH}=\text{C}(\text{CH}_3)_2$ and R- $\text{CH}=\text{CH}_2$ groups will represent 74% and 22% respectively of the
9 overall reaction.

10
11 **Gas phase product studies.** The products of the reactions of OH radicals with the unsaturated
12 alcohols at room temperature and 760 Torr of air were monitored using FT-IR spectroscopy.
13 The photolysis of H_2O_2 at 254 nm was used to generate OH radicals. Reaction mixtures
14 consisted of $(1.2 - 9.1) \times 10^{13}$ molecule cm^{-3} of unsaturated alcohols and $(0.32 - 5.7) \times 10^{14}$
15 molecule cm^{-3} of H_2O_2 . A set of three experiments was performed for each unsaturated
16 alcohol. The products of the reactions have been assigned using IR reference spectra when
17 available. Gas phase formation yields for the oxidation products were obtained after
18 correction of their concentration time-profiles for dilution and for loss by secondary reactions
19 with OH radicals. The observed products from the three unsaturated alcohols and their
20 corresponding reaction rate coefficients with OH (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are the following:
21 formaldehyde (8.5×10^{-12}), formic acid (4.5×10^{-13}), carbon monoxide (2.8×10^{-12}),
22 glycolaldehyde (8×10^{-12}), 2-butanone (1.2×10^{-12}), methanol (9×10^{-13}), acetone (1.8×10^{-13})
23 and 6-methyl-5-hepten-2-one (1.57×10^{-10}). These rate coefficient values were taken from the
24 IUPAC recommendation,³³ except for 6-methyl-5-hepten-2-one, which is from Smith et al.⁴⁹
25 Corrections of concentration time-profiles of the oxidation products formed have been applied

1 according to the formula given by Atkinson et al.⁵⁰ Preliminary tests were conducted in order
2 to observe the behaviour of the unsaturated alcohols in the absence of any oxidants and
3 possible oxidation products, which might be formed. The results showed that under these
4 conditions, consumption of the unsaturated alcohols was negligible. Figure 7 shows the IR
5 spectra of linalool (Panel A), and a mixture of linalool and H₂O₂ at the start of the reaction
6 (Panel B). Panel C shows the IR spectrum after 4 hours reaction (linalool and H₂O₂ subtracted
7 from the IR global spectrum). The reference spectra of acetone, formic acid, glycolaldehyde
8 and 6-methyl-5-hepten-2-one are displayed in the Panels D, E, F and G, respectively. Panel H
9 shows the residual spectrum after subtraction of reactants and all identified products.

10 Due to secondary reactions, the yields of gas phase products do not scale linearly with the loss
11 of linalool over the whole experimental time. Therefore, the yields of products were obtained
12 by plotting the gas phase product concentrations versus the linalool consumption in the early
13 stages of the reaction, as shown in Figure 8. The molar product yields were derived from the
14 least-square analysis of the data and are summarized in Tables 4(a-c). The major products
15 identified from the OH-initiated reaction of linalool were acetone (34 ± 1)%, glycolaldehyde
16 (14 ± 1)% and 6-methyl-5-hepten-2-one (10 ± 2)%. The indicated errors arise from the
17 average of yields obtained from the three individual experiments. For the reaction of OH with
18 6-methyl-5-hepten-2-ol, acetone was identified as the major product with a yield of (21 ± 2)%.
19 Other minor products identified in the system were formic acid (4.2 ± 0.7)%, formaldehyde
20 (0.7 ± 0.4)% and carbon monoxide (1.2 ± 0.6)%. The OH-initiated oxidation of 3-methyl-1-
21 penten-3-ol produced 2-butanone (41 ± 6)% and glycolaldehyde (30 ± 4)% as major products
22 with formic acid (2.2 ± 0.9)%, formaldehyde (9 ± 4)% and carbon monoxide (2.5 ± 0.3)% as
23 minor products.

24 A number of product studies on the OH radical initiated oxidation of linalool have been
25 reported, however, the previous studies were carried out in the presence of NO_x.^{3,17,24}

1
2
3 1 Therefore, this work reports for the first time the yields of products from the OH initiated
4
5 2 oxidation in the in the absence of NO_x. The OH initiated oxidations of 6-methyl-5-hepten-2-
6
7
8 3 ol and 3-methyl-1-penten-3-ol have not previously been reported.

9
10 4 The kinetic data leads to the prediction that addition of OH to the (R-CH=C(CH₃)₂) group is
11
12 5 likely to dominate over reaction at (R-CH=CH₂) with a ratio of around 59% / 36%. The
13
14 6 proposed reaction schemes following OH addition at the R-CH=CH₂ and R-CH=C(CH₃)₂ sites
15
16 7 in linalool are shown in Figures 9a and 9b, respectively. 6-Methyl-5-hepten-2-one and
17
18 8 glycolaldehyde are expected to be formed following OH attack at the =CH₂ position of the R-
19
20 9 CH=CH₂ double bond as shown in reaction channel (1) of Figure 10c. Addition of OH to the
21
22 10 RCH= position of the double bond leads to the generation of formaldehyde and 2,6-dimethyl-
23
24 11 2-hydroxy-5-hepten-1-one, channel (2). The low yield of HCHO (2.8%) indicates that OH
25
26 12 radical addition at the =CH₂ position, channel (1), is dominant. This result is consistent with
27
28 13 the observation that addition of radical species normally occurs at the least substituted carbon
29
30 14 atom of a double bond in an alkene, and is in agreement with the low HCHO yield reported
31
32 15 previously by Shu et al.³ Addition of the OH radical to the R-CH=C(CH₃)₂ group of linalool
33
34 16 is expected to produce acetone and its co-product 4-hydroxy-4-methyl-5-hexen-1-al (or 2-
35
36 17 ethenyl-2-methyl-5-hydroxytetrahydrofuran) by both channels (1) and (2), Figure 9b. The
37
38 18 yield of 4-hydroxy-4-methyl-5-hexen-1-al was not quantified, since a reference spectrum of
39
40 19 this compound was not available. Its formation yield has been estimated at (75 ± 10)% by Lee
41
42 20 et al.²⁴, (46 ± 11)% by Shu et al.³ and in the range 18-43% by Calogirou and Kotzias¹⁷ in
43
44 21 studies performed in the presence of NO_x.

45
46 22 Acetone is formed from decomposition of the alkoxy radical generated following addition of
47
48 23 OH to either carbon atom of the R-CH=C(CH₃)₂ double bond in linalool, while
49
50 24 glycolaldehyde is the major product generated by addition of OH to the R-CH=CH₂ group,
51
52 25 Figures 9b and 9a respectively. Assuming that the peroxy radicals produced in the reaction of

1 OH with linalool are quantitatively converted to the corresponding alkoxy radicals, then the
2 ratio of the yields of acetone (34%) to glycolaldehyde (14%) of 2.4 represents the relative
3 importance of the addition of OH to the R-CH=C(CH₃)₂ and R-CH=CH₂ sites in linalool. The
4 kinetic data suggests that the ratio should be about 1.6 (59% / 36%). However, the relatively
5 low yields for the formation of both acetone and glycolaldehyde indicate that conversion of the
6 peroxy radicals to the corresponding alkoxy radicals by reaction with alkyl peroxy or hydro
7 peroxy radicals is relatively low.

8 **Aerosol formation.** The relatively rapid reaction of OH radicals with the unsaturated alcohols
9 means that investigations on SOA formation in these reactions are simplified compared to
10 studies of the corresponding reactions with O₃. The photolyses were carried out using only
11 one lamp in order to reduce the influence of UV light on the SOA formation rate,⁵¹ and to
12 limit the increase of temperature during the reactions which could have an impact on gas-
13 particle partitioning and the chemical mechanism.⁵²⁻⁵⁴ Under our experimental conditions,
14 SOA formation was observed 5 to 20 minutes after photolysis commenced. Figure 10 shows
15 an example of the particle size distribution over the course of the reaction. Growth of the
16 particles by condensation reaches a maximum, and then decreases due to coagulation and wall
17 loss.

18 The SOA yield from the OH radical initiated oxidation of 3-methyl-1-penten-3-ol was in the
19 range 0.8-1.5% under our experimental conditions, while the corresponding reaction of 6-
20 methyl-5-hepten-2-ol led to a SOA formation yield of 0.2-0.8%. Experiments carried out on
21 the oxidation of linalool led to SOA formation yields ranging from 14 to 52%. Thus,
22 formation of SOA from the oxidation of linalool is considerably more efficient than for the
23 other two unsaturated alcohols investigated. It is of interest to compare the SOA yield of 0.8-
24 1.5% obtained for the oxidation of 3-methyl-1-penten-3-ol to that of ~ 0.1% reported for the
25 structurally similar molecule 2-methyl-3-buten-2-ol ((CH₃)₂C(OH)CH=CH₂).⁵⁵ Previous

1 studies on SOA formation from the OH-initiated oxidation of linalool have been carried out in
2 the presence of NO_x, and the reported mass yields were in the range 4 to 18%.^{18,20,24,25} These
3 yields are considerably lower than found in this work, however, the SOA mass yields
4 obtained from NO_x-free experiments has been found to be significantly higher than in
5 experiments conducted in the presence of NO_x. For example, a NO_x-dependence for SOA
6 formation has previously been observed for the OH-initiated reaction of isoprene⁵⁶ and α -
7 pinene.⁵⁷ It has been suggested that for low NO_x-conditions, peroxy radicals will react with
8 RO₂ or HO₂ radicals rather than NO, leading to formation of organic acids with low volatilities
9 which will increase SOA mass yields.⁵⁸

10

11 **5. Atmospheric implications**

12 The rate coefficients obtained in this study for the reactions of three unsaturated alcohols with
13 ozone and OH radicals can be used to estimate their tropospheric lifetimes with respect to
14 reaction with these oxidants. Using the 24 hour average atmospheric concentration of ozone,
15 7×10^{11} molecule cm⁻³,⁵⁹ and the 12 hour daytime average concentration of OH radicals, $2 \times$
16 10^6 molecule cm⁻³,⁶⁰ the calculated lifetimes due to reaction with OH radicals are: 49 min, 1.4
17 hours and 2.2 hours for linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol
18 respectively, while those due to reaction with ozone are: 58 min, 1.1 hours and 3 days for
19 linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol respectively. Hence, linalool, 6-
20 methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol have relatively short lifetimes and will be
21 degraded close to their emission sources. Long-range transport of these compounds will be of
22 little importance. The atmospheric degradation of unsaturated alcohols by reaction with OH
23 radicals and ozone will lead to formation of various carbonyl compounds, which may
24 influence the composition of the lower troposphere. Low molecular weight carbonyl
25 compounds such as acetone, formaldehyde, hydroxyacetone and glycolaldehyde will be

1 degraded by photolysis and reaction with OH radicals with atmospheric lifetimes estimated
2 from a few hours to a few days.⁶¹⁻⁶⁴ Acetone has been recognized as a source of HO_X in the
3 upper troposphere and may have an effect on the stratospheric ozone budget.⁶¹
4 Hydroxyacetone and glycolaldehyde have been detected in both gas and particulate phases in
5 various forest environments, and it is likely that a significant fraction of these compounds
6 might arise through the degradation of BVOCs.⁶⁵
7 In general, the three unsaturated alcohols investigated in this work are unlikely to make a
8 significant contribution to SOA formation in the atmosphere through reaction with ozone or
9 OH radicals. However, it is possible that the reaction of linalool with OH under low NO_X
10 conditions close to emission sources such as forested areas could constitute a source of
11 condensed organic material that might be rapidly produced due to the high reactivity of
12 linalool. A detailed examination of SOA formation from the OH-initiated oxidation of
13 linalool as a function of NO_X under atmospheric conditions would be of interest.

14 15 **Associated Content**

16 Data obtained in the absolute measurements of the reaction of ozone with the studied alcohols
17 and the SOA formation yield from the ozone and OH reactions are attached. O₃- and OH-
18 initiated gas phase oxidation mechanisms are also included. Plots of the gas phase oxidation
19 products from the ozonolysis reaction of linalool and the SOA mass concentration versus the
20 time from the OH reaction with linalool are showed. This material is available free of charge
21 via the Internet at <http://pubs.acs.org>.

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Table 1. Reactions with O₃, 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	N ^o of runs	T (K)	($k/k_{\text{Ref.}} \pm 1\sigma$)	($k \pm 1\sigma$) (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
$k = (4.1 \pm 1.0) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$					
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
$k = (3.7 \pm 1.2) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$					
3-methyl-1-penten-3-ol	propene	3	294 ± 2	0.50 ± 0.01	(5.0 ± 0.6) × 10 ⁻¹⁸
	$k = (5.0 \pm 0.6) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$				

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Table 2a. Reaction of linalool with O₃: gas phase product yields (Cyclohexane used as OH scavenger).

linalool + O ₃	
Acetone	35 ± 6
Formaldehyde	32 ± 6
Hydroxyacetone	28 ± 5
<i>Carbon balance</i>	22 ± 4

Table 2b. Reaction of 6-methyl-5-hepten-2-ol with O₃: 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
<i>Carbon balance</i>	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-hydroxypentanal was quantified using 4-pentanal as a surrogate by HPLC-UV (see text).

Table 2c. Reaction of 3-methyl-1-penten-3-ol with O₃: 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
<i>Carbon balance</i>	37 ± 2

Table 3. 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	N ^o of runs	T (K)	($k/k_{\text{Ref.}} \pm 1\sigma$)	($k \pm 1\sigma$) ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
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
			$k = (1.7 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
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
			$k = (1.0 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
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
			$k = (6.2 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		

Table 4a. Reaction of linalool with OH radicals: gas phase product yields (H_2O_2 used as OH precursor).

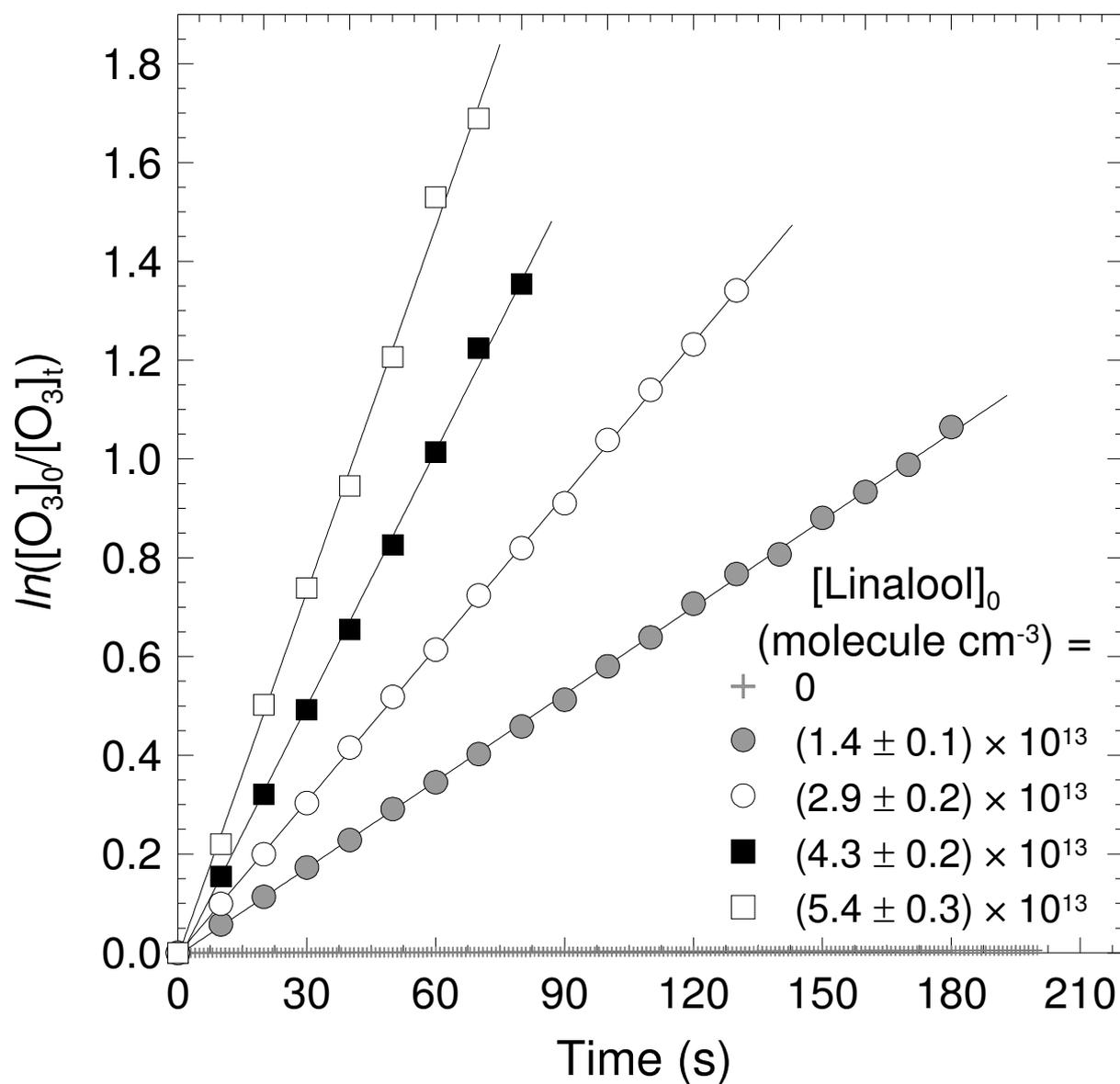
linalool + OH	
Acetone	34 ± 1
Glycolaldehyde	14 ± 1
6-methyl-5-hepten-2-one	10 ± 2
Formic acid	5 ± 2
Formaldehyde	2.8 ± 0.4
Carbon monoxide	2.1 ± 0.8
<i>Carbon balance</i>	22 ± 2

Table 4b. 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
<i>Carbon balance</i>	8 ± 1

Table 4c. 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
<i>Carbon balance</i>	40 ± 6



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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.

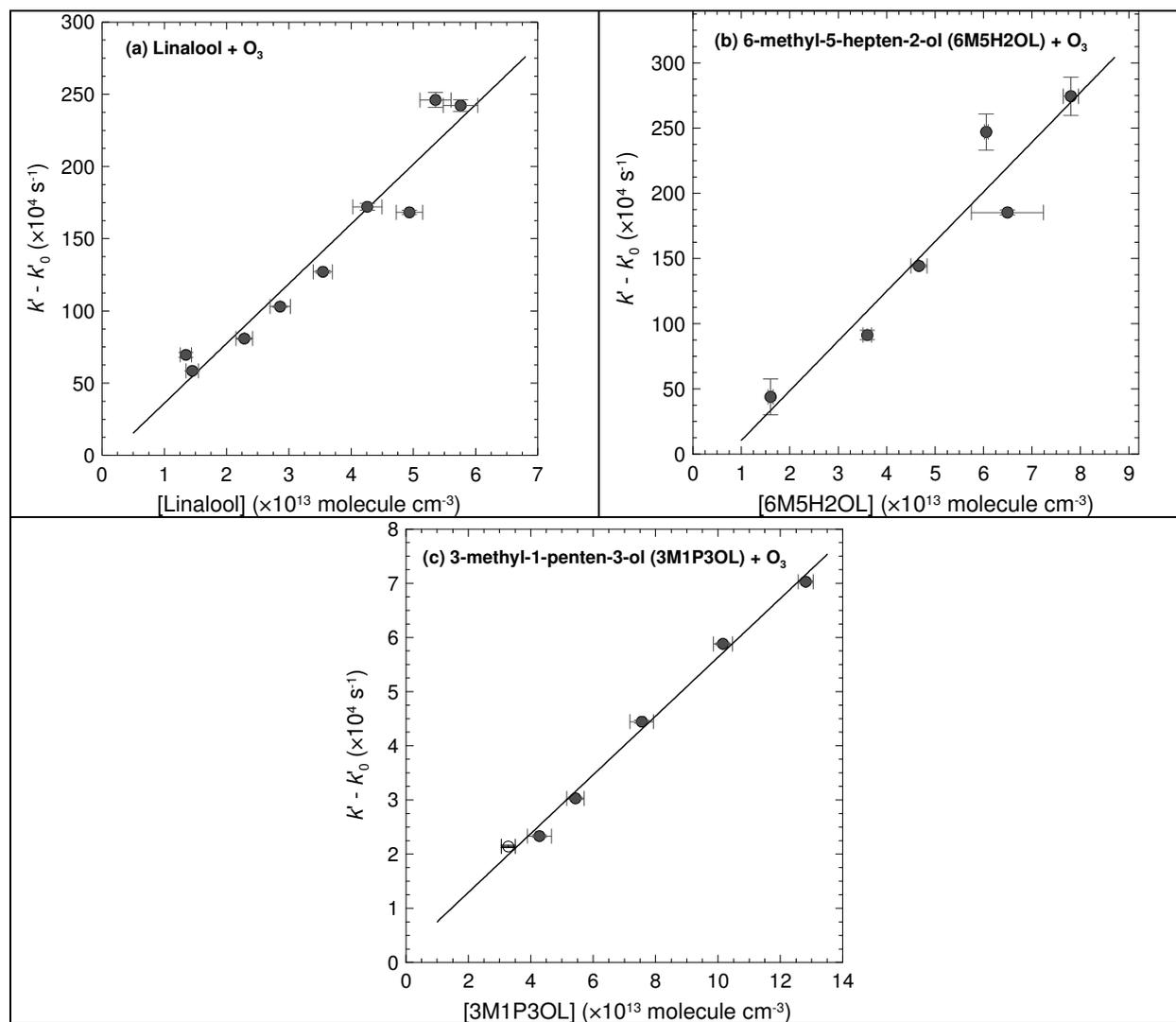


Figure 2. Reaction of O₃ with linalool (a), 6-methyl-5-hepten-2-ol (b) and 3-methyl-1-penten-3-ol (c): absolute rate kinetic data (Experiments conducted in the presence of an excess of cyclohexane are represented with filled circles while that conducted without cyclohexane is showed with the unfilled symbol).

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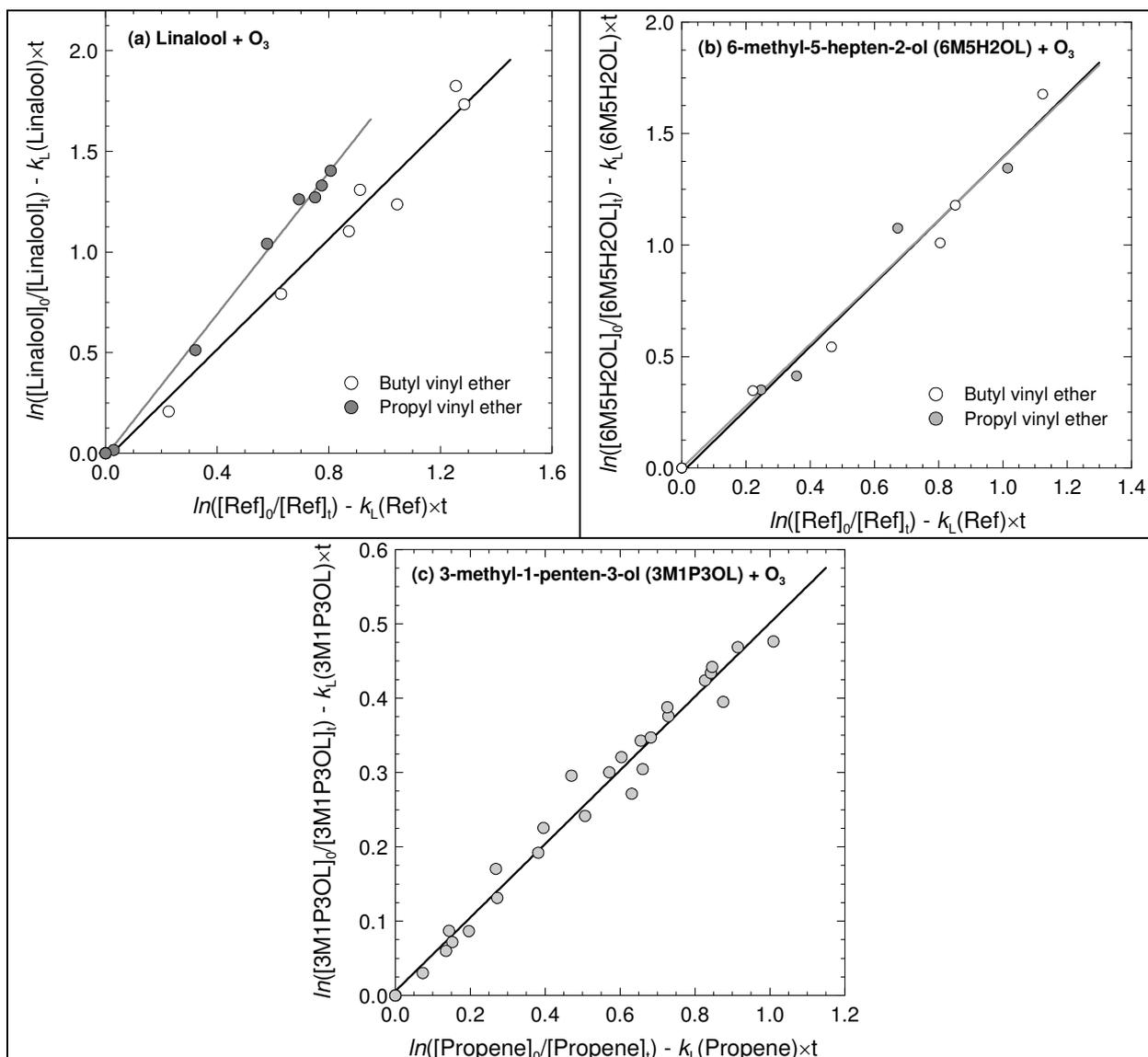


Figure 3. Reaction of O₃ with linalool (a), 6-methyl-5-hepten-2-ol (b) and 3-methyl-1-penten-3-ol (c): relative rate kinetic data using butyl vinyl ether, propyl vinyl ether and propene as organic references.

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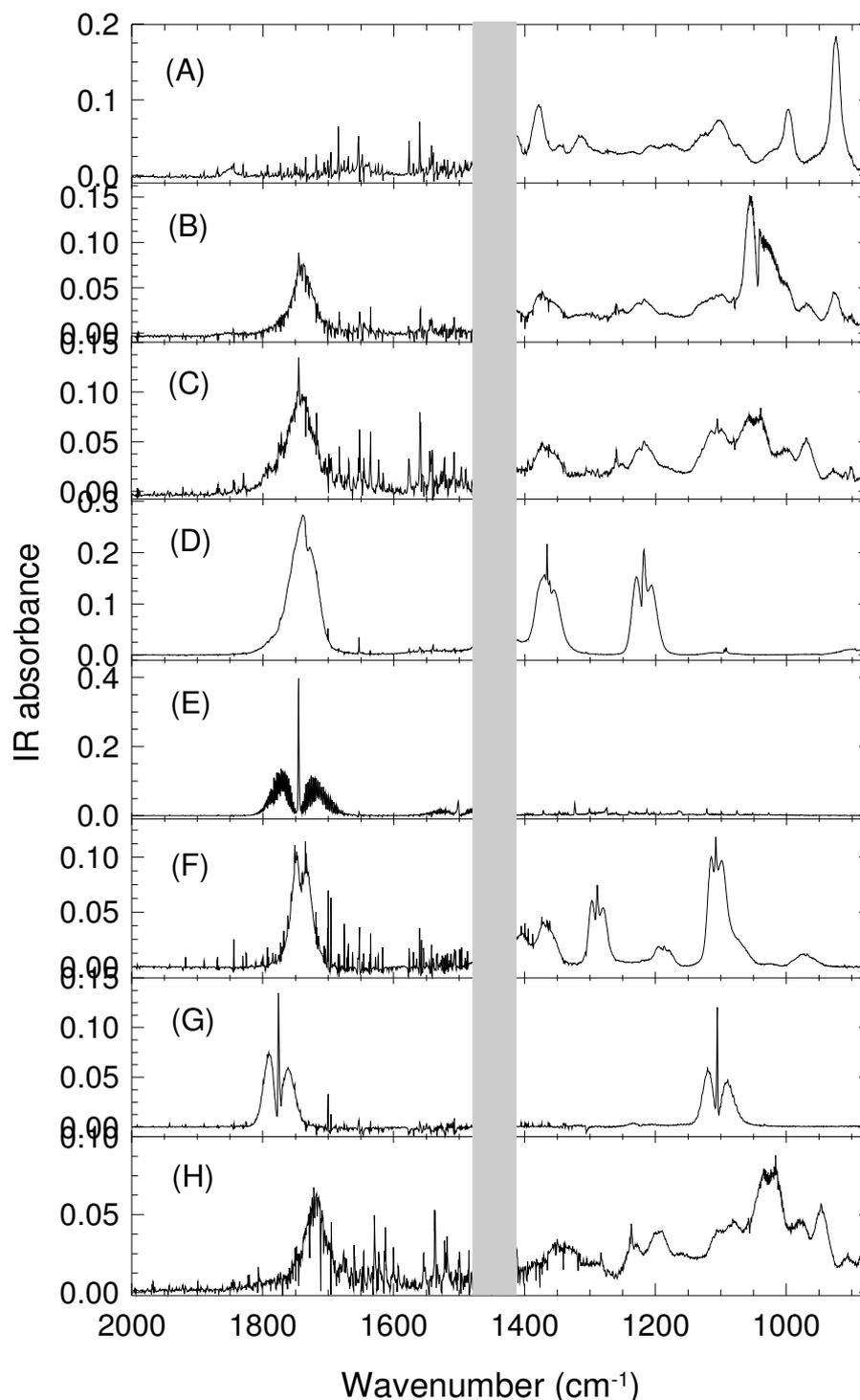
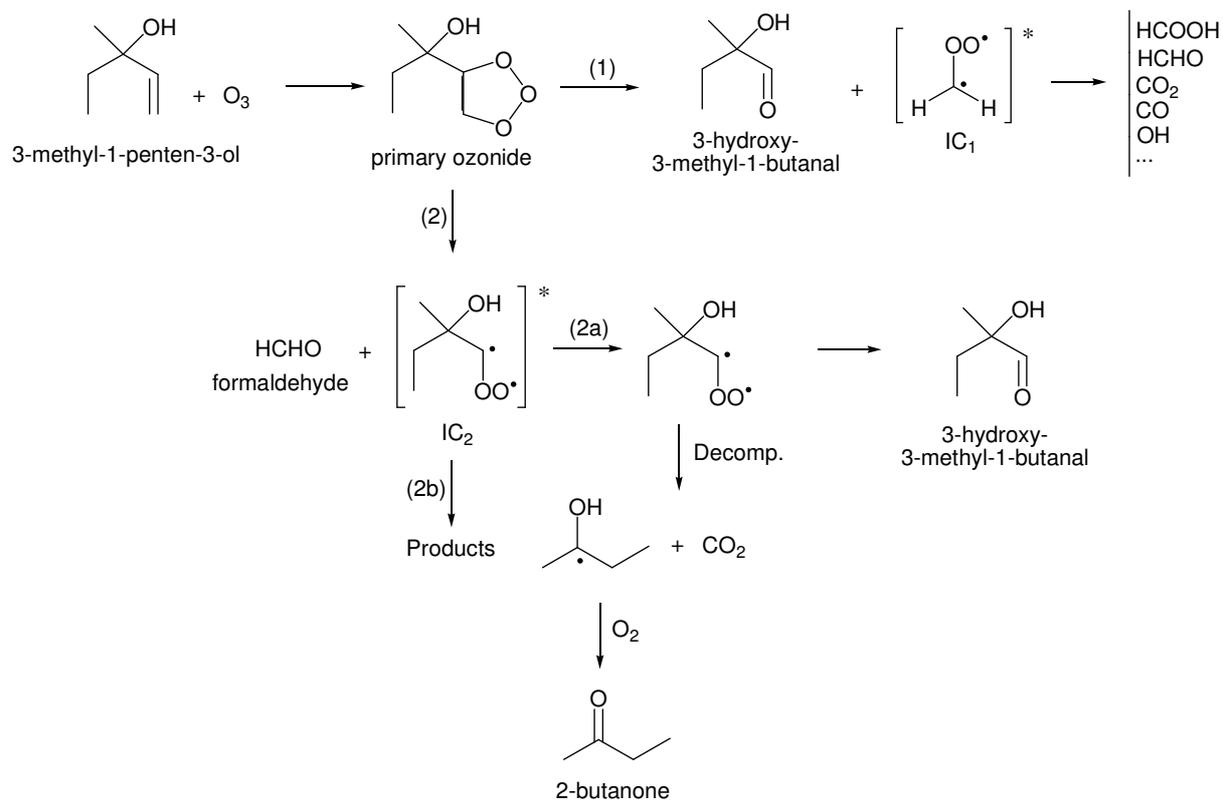


Figure 4. Reaction of linalool with O_3 (in the presence of an excess of cyclohexane). Cyclohexane was subtracted from all the IR spectra shown here. Reference IR spectrum of linalool (Panel A), IR spectrum of a mixture of linalool and O_3 at the start of the experiment (Panel B), IR spectrum of a mixture of linalool and O_3 after 2 hours of reaction (Panel C, linalool and O_3 are subtracted from the global spectrum); reference IR spectra of acetone (Panel D), formaldehyde (Panel E), hydroxyacetone (Panel F) and formic acid (Panel 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) (Panel H). The grey overlap area represents IR band saturation due to the excess of cyclohexane used as OH scavenger.



33 **Figure 5.** Reaction of 3-methyl-1-penten-3-ol with O₃: proposed mechanism scheme.

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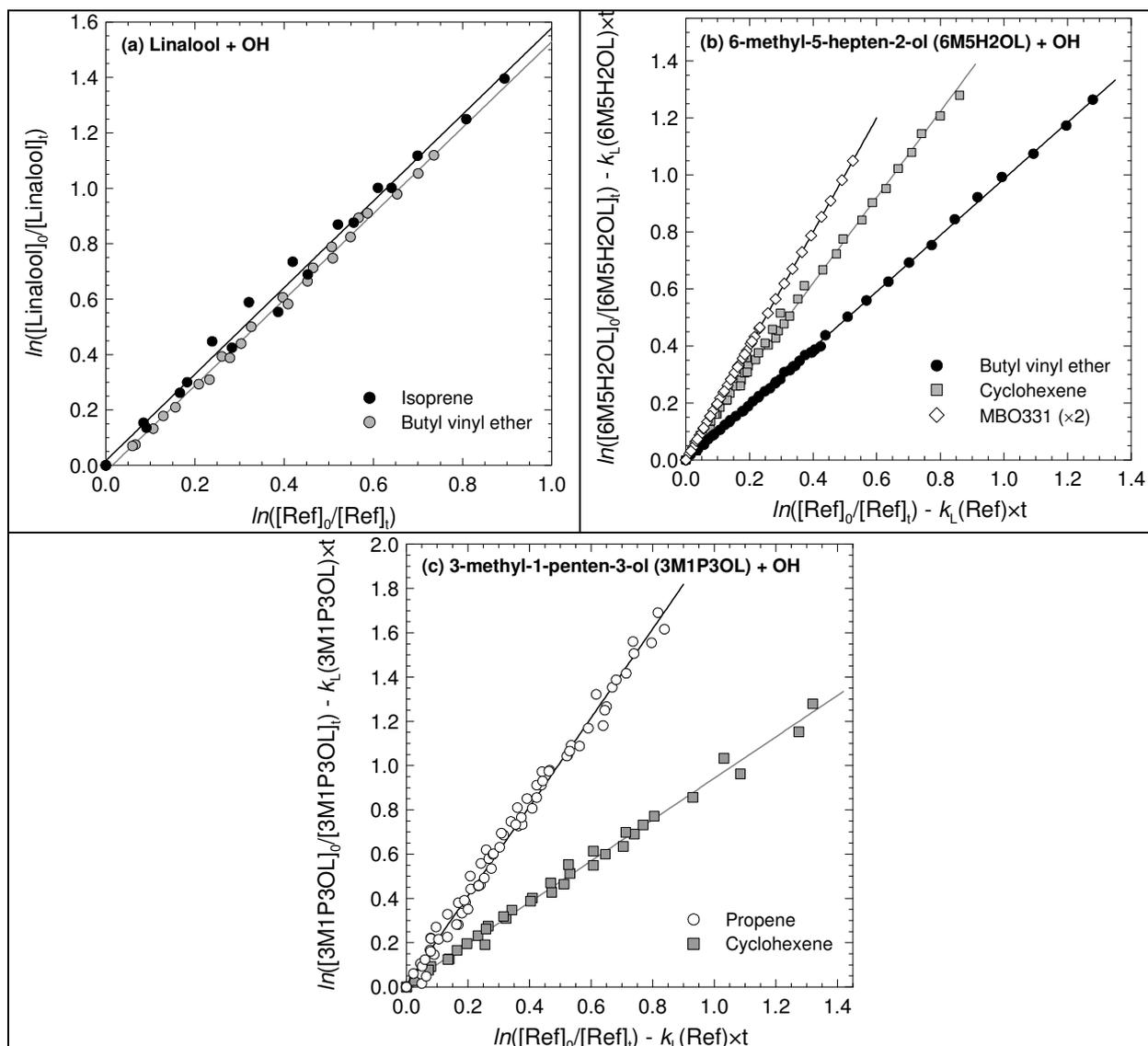


Figure 6. Reaction of OH radicals with linalool (a), 6-methyl-5-hepten-2-ol (b) and 3-methyl-1-penten-3-ol (c): relative rate kinetic data using butyl vinyl ether, isoprene, 3-methyl-3-buten-1-ol (MBO331), cyclohexene and propene as organic references.

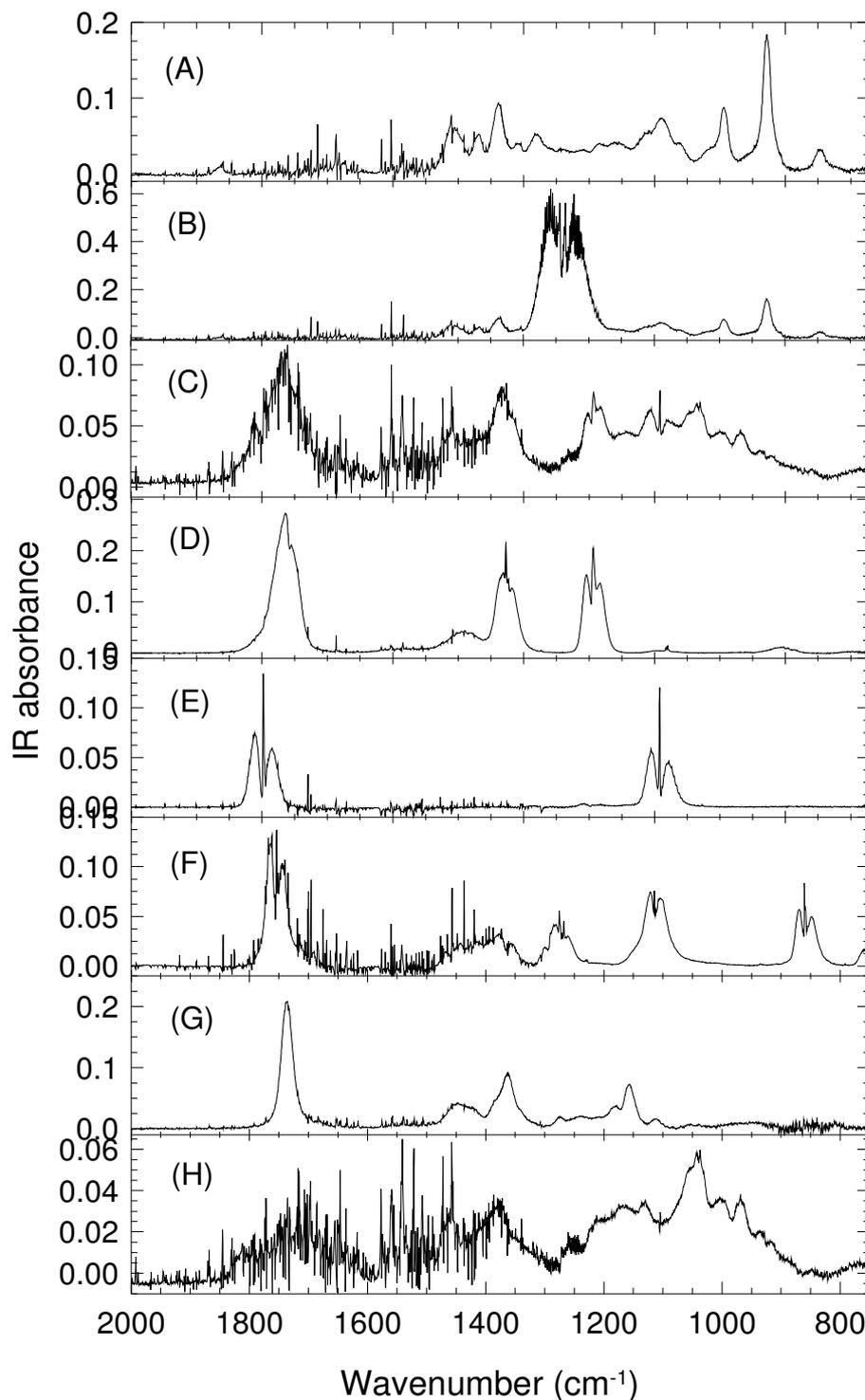


Figure 7. Reaction of linalool with OH (H_2O_2 used as OH precursor): Reference IR spectra of: linalool (Panel A), IR spectrum of mixture linalool and H_2O_2 at the start of the experiment (Panel B), IR spectrum of a mixture of linalool and H_2O_2 after 4 hours reaction (Panel C), linalool and H_2O_2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

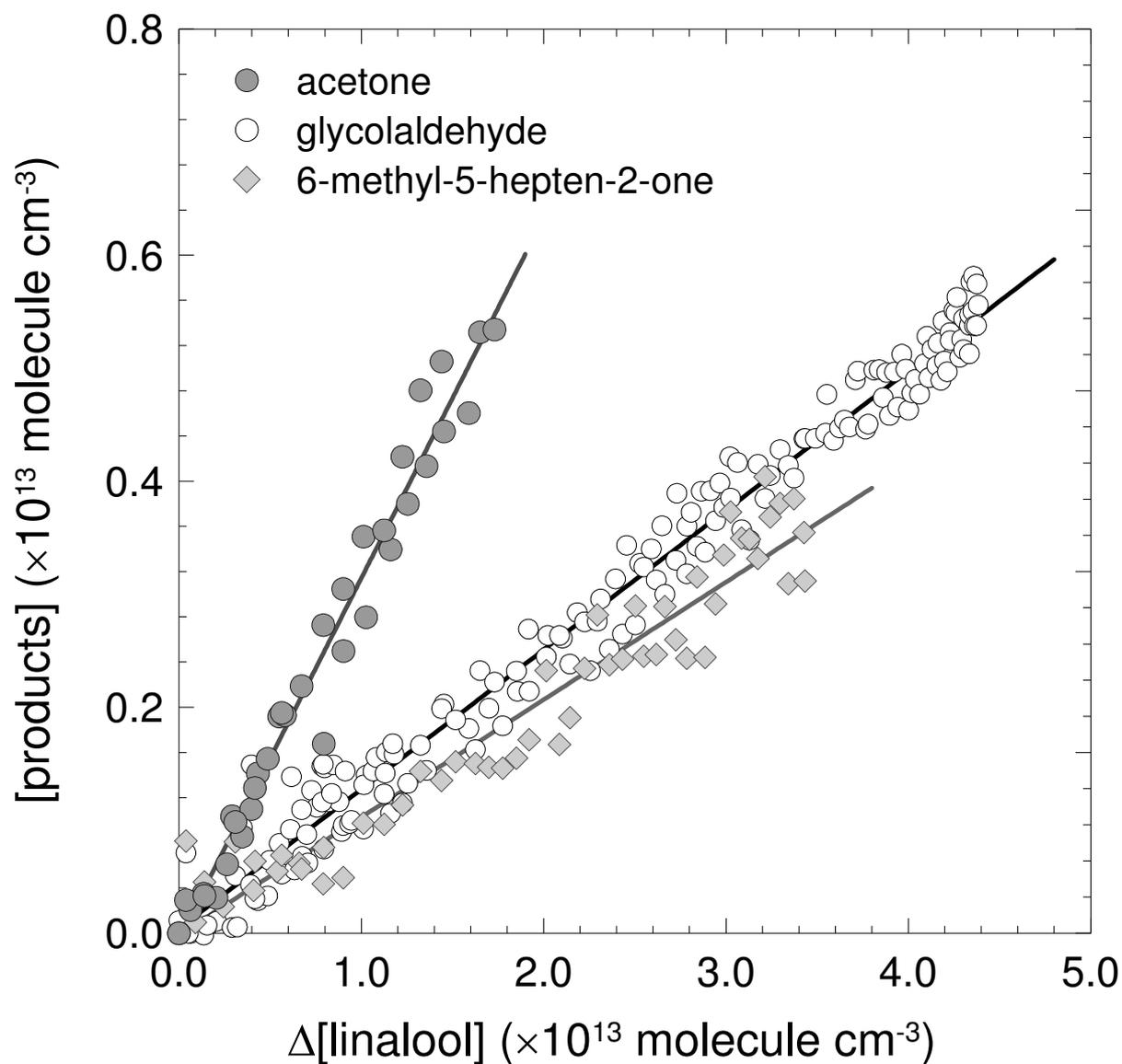
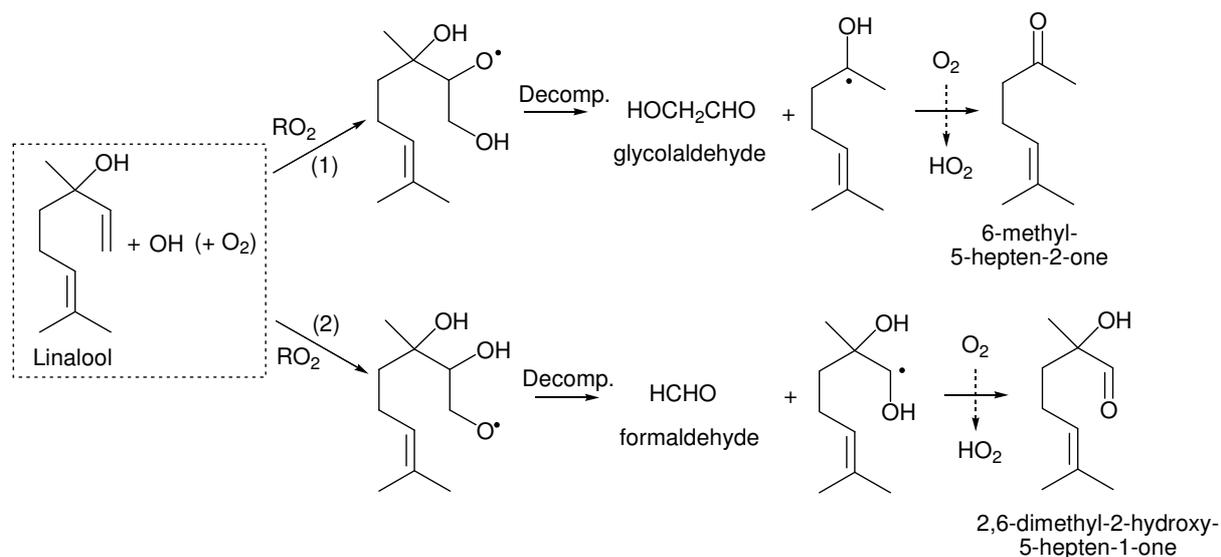
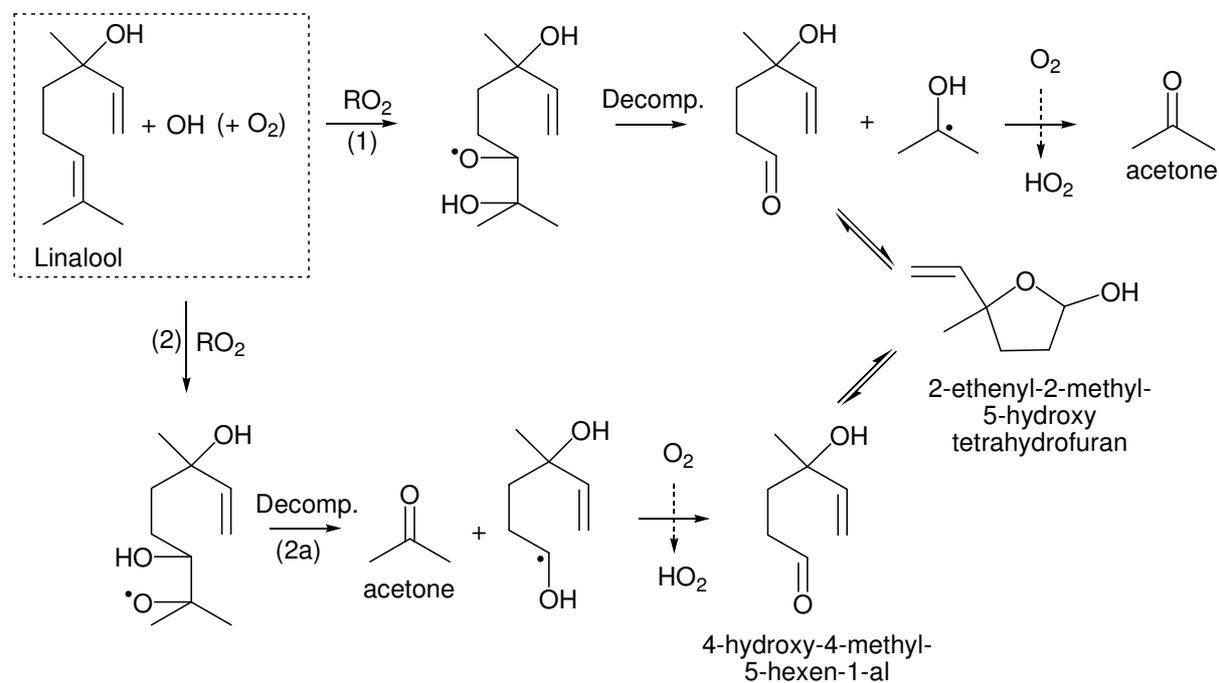


Figure 8. Reaction of linalool with OH (H_2O_2 used as OH precursor): gas phase product yields.



25 **Figure 9a.** Reaction of linalool with OH (in the absence of NO_x): proposed mechanism
26 scheme for OH attack at the R-CH=CH₂ double bond.



55 **Figure 9b.** Reaction of linalool with OH (in the absence of NO_x): proposed mechanism
56 scheme for OH attack at the R-CH=C(CH₃)₂ double bond.

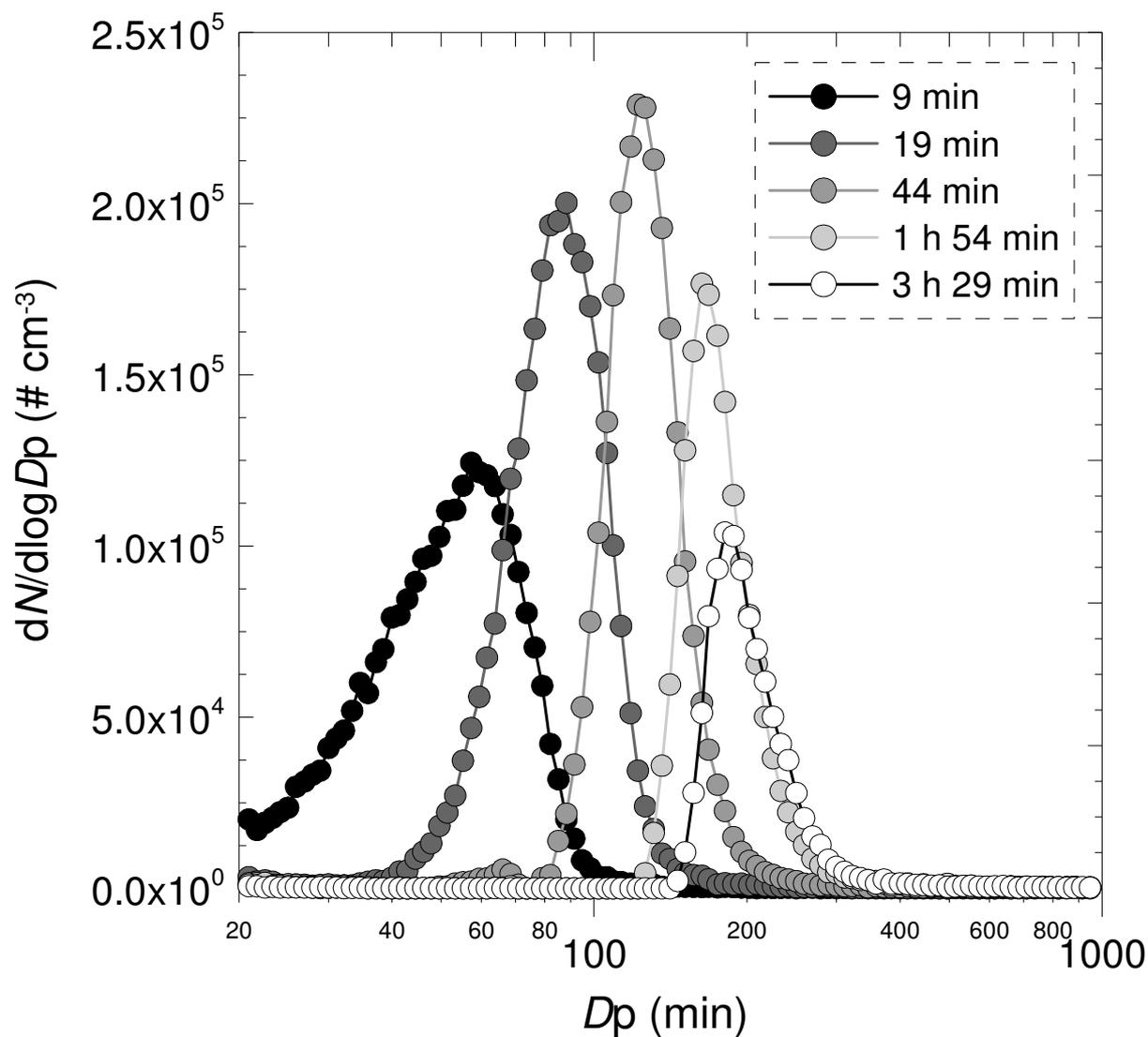


Figure 10. Reaction of linalool with OH (in the absence of NO_x): secondary organic aerosol particle size distribution obtained over the course of the reaction.

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