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# Atmospheric sink of (*E*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol: Rate coefficients and mechanisms of the OH-radical initiated degradation

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## Abstract

A kinetic study of the gas-phase reactions of OH radicals with three unsaturated biogenic alcohols (*E*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol has been performed. The rate coefficients obtained are (in units of $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$): $k_1$(OH + *(E)*-$CH_2(OH)CH_2CH{=}CHCH_2CH_3$) = (1.14 ± 0.14), $k_2$(OH + *(Z)*-$CH_2(OH)CH_2CH{=}CHCH_2CH_2CH_3$) = (1.28 ± 0.23) and $k_3$(OH + *(Z)*-$CH_2(OH)CH_2CH{=}CHCH_2CH_2CH_2CH_3$) = (1.49 ± 0.35). In addition, a product study on the reactions of OH with (*E*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol is reported. All the experiments were performed at (298 ± 3) K and 1 atm of $NO_x$-free air in a 1080 L photoreactor with in situ FTIR detection of organics.

This work constitutes the first kinetic study of the reactions of OH radicals with (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol as well as the first determination of the fate of the hydroxy alkoxy radicals formed in the title reactions.

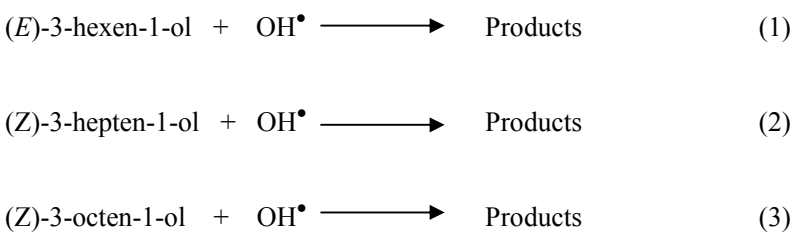
An analysis of the available rates of addition of OH and Cl to the double bond of different unsaturated alcohols at 298 K has shown that they can be related by the expression $\log k_{OH} = (0.29\pm0.04) \log k_{Cl} - 10.8$. The atmospheric lifetimes of the alcohols studies were estimated to be

around one hour for reaction with OH radicals. The products formed in the title reactions are mainly carbonylic compounds that can contribute to formation of ozone and PANs-type compounds in the troposphere.

## Introduction

Emissions of biogenic volatile organic compounds (BVOCs) represent a substantial fraction of the total amount of compounds emitted into the atmosphere. Unsaturated alcohols such as *(E)*-3-hexen-1-ol, *(Z)*-3-hepten-1-ol, and *(Z)*-3-octen-1-ol are particularly important BVOCs predominantly emitted from several plant species.[1-3]
*(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol are used in the industry as solvents and are emitted in high-temperature alfalfa drying.[4] These unsaturated alcohols, in combination with other compounds, can be used as biopesticides to control some mosquito species.[5] Consequently, large amounts of these organics are emitted daily into the atmosphere where they are degraded by physical and chemical processes. In order to assess the impact of these compounds on air quality, detailed studies on their reactivity toward the main atmospheric oxidants as well as the resulting degradation products are required.

In this study we present relative rate coefficients for the reactions of OH radicals with three unsaturated alcohols (*(E)*-3-hexen-1-ol, *(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol):




In addition, product studies on the reactions of OH radicals with (*E*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol in the absence of $NO_x$ have been performed for the first time.

Although, many kinetic and product studies for the reactions of the main tropospheric oxidants with saturated alcohols have been reported in the literature[6-8], only a few studies for the unsaturated alcohols have been reported, and these have been mainly restricted to butenols and a few pentenols.[8] The kinetic and product distribution data available in the literature for C6, C7 and C8 alcohols is very scant. The kinetics of the reaction of OH radicals with *(Z)*-3-hexen-1-ol has been investigated using relative[9] and absolute kinetic methods.[10,11] A rate coefficient of the reaction of OH radicals with *(Z)*-2-hexen-1-ol was determined by Davis and Burkholder[11] in the temperature range 243-404 K and at pressures between 20 and 100 Torr. More recently, a relative kinetic study on the

reaction of OH radicals with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol at 298 K and atmospheric pressure using GC-FID has been reported by our group.[12]

The reactions of $NO_3$ and $N_2O_5$ with a series of hexenols have been studied in a low-pressure flow reactor with accompanying relative determinations in a collapsible Teflon chamber at 1 atm.[13] Atkinson et al.[9] have reported a relative kinetic determination of the rate coefficient for the reaction of $NO_3$ with (Z)-3-hexen-1-ol. Grosjean et al.[14] and Atkinson et al. [9] have reported rate coefficients for the reaction of $O_3$ with (Z)-3-hexen-1-ol using an absolute and relative techniques, respectively.

Most past studies on the Cl-atom initiated degradation of unsaturated alcohols have been limited to ≤C5 compounds.[15-19] However, recently we have reported rate coefficients for the reactions of Cl atoms with some C6, C7 and C8 unsaturated alcohols determined using a relative kinetic method.[20]

In addition to the kinetic study, we present i) a correlation between the reactivity of the unsaturated alcohols toward OH radicals with that of Cl atoms toward the same compounds, ii) an analysis of the products formed in the OH-radical initiated degradation of the unsaturated alcohols under $NO_x$-free conditions, and iii) possible atmospheric implications of the reactions studied.

This kinetic and product study on the OH-radical initiated oxidation of three $C_6$, $C_7$, and $C_8$ unsaturated alcohols will help in assessing the contribution of these compounds to the oxidizing capacity of the atmosphere, tropospheric ozone production, and secondary organic aerosol (SOA) formation.

## Experimental

A quartz-glass reaction chamber of 1080 L was used to perform the experiments at (298 ± 2) K and a total pressure of (760 ± 10) Torr synthetic air. The reactor has been described in detail previously.[21]

The reactor can be evacuated to $10^{-3}$ Torr using a turbo-molecular pump backed by a double stage rotary fore pump. Mixing fans are mounted inside the chamber for homogeneous mixing of the reactants. 32 low-pressure mercury vapor lamps mounted in parallel (Philips TUV 40W; $\lambda_{max}$ = 254 nm) were used for radical precursor photolysis. The light intensity and hence the radical production rate can be regulated by adjusting the number of lamps irradiating the chamber.

A multiple pass White-type mirror system, with a base length of (5.91 ± 0.01) m, is mounted inside the chamber. The mirror system was operated at 82 traverses resulting in a total optical path length of (484.7 ± 0.8) m. A Nicolet Nexus FT-IR spectrometer with a mercury-cadmium-telluride (MCT) detector coupled to the mirror system was used to monitor reactants and products in the spectral range 4000 – 700 $cm^{-1}$ with a resolution of 1 $cm^{-1}$.

Photolysis of hydrogen peroxide ($H_2O_2$) was used as the OH radical precursor:

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet} \quad (4)$$

Reactants and products were quantified using calibrated reference spectra from the collection of infrared spectra available at the University of Wuppertal. In the product studies mixtures of $H_2O_2$-alcohol-air were irradiated for periods of 20 minutes and infrared spectra were recorded with the FTIR spectrometer. In a typical experiment, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15-20 such spectra were collected.

The following frequencies (in $cm^{-1}$) were used to monitor the reactants: *(E)*-3-hexen-1-ol at 1050.8, 1385.8 and 3619.3, *(Z)*-3-hepten-1-ol 1053.7 and 3616.5, *(Z)*-3-octen-1-ol 1054.1 and 3616.8, isobutene at 889.2 and *(E)*-2-butene at 2948.5 and 963.1.

Rate coefficients for the competitive reactions of OH radicals with unsaturated alcohols (*(E)*-3-hexen-1-ol, *(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol) were determined by the relative kinetic method using two different references compounds (*(E)*-2-butene and isobutene):

$$OH^{\bullet} + \text{Alcohol} \rightarrow \text{Products} \quad (5)$$

$$OH^{\bullet} + \text{Reference} \rightarrow \text{Products} \quad (6)$$

If the alcohol and the reference compound are lost only by reactions (5) and (6) it can be shown that:

$$\ln\left\{\frac{[\text{Alcohol}]_0}{[\text{Alcohol}]_t}\right\} = \frac{k_{Alcohol}}{k_{\text{Reference}}} \ln\left\{\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right\} \quad (\text{I})$$

where, $[Alcohol]_0$, $[Reference]_0$, $[Alcohol]_t$ and $[Reference]_t$ are the concentrations of the alcohol and the reference compound at times $t$=0 and $t$, respectively, and $k_{Alcohol}$ and $k_{Reference}$ are the rate coefficients of reactions (5) and (6), respectively.

The initial concentration of unsaturated alcohols ranged from (8-10) ppmV for (E)-3-hexen-1-ol, and (7-9) ppmV for (Z)-3-hepten-1-ol and (Z)-3-octen-1-ol. The initial concentrations of the reference compounds ranged from 4 to 5 ppmV.

To check that the only loss process of the alcohol and the reference compounds in the reaction systems is reaction with OH radicals, different tests were performed. Mixtures of $H_2O_2$ in air with the alcohol and the reference compound were prepared and allowed to stand in the dark for two hours. In all cases, dark reactions of the organic species with $H_2O_2$ were negligible. Furthermore, to test for possible photolysis of alcohols, mixtures the reactants were irradiated for 30 minutes in the absence of the OH radical precursor, using the output of all the lamps surrounding the chamber. No significant photolysis of any of the reactants was observed. In addition, tests were performed to assess possible loss of the reactants via deposition to the chamber walls. Wall deposition of the three

alcohols studied and the reference compounds used were negligible over the time span of the experiments with $k_{wall} < 10^{-5}$ $s^{-1}$ for all compounds.

## Materials

The following chemicals, with purities as stated by the supplier, were used without further purification: synthetic air (Air Liquide, 99.999%), nitrogen (Air Liquide, 99.999%), isobutene (Messer Griesheim, 99 %), $H_2O_2$ (Interox, 85%), (*E*)-2-butene (Messer Griesheim, 99 %), (*E*)-3-hexen-1-ol (Alfa Aesar, 97%), (*Z*)-3-hepten-1-ol (Alfa Aesar, 97%) and (*Z*)-3-octen-1-ol (Alfa Aesar, 95%). Impurities in the reactants at the 3-5% level were barely visible in the infrared spectra and thus do not constitute a problem for both the kinetic and product analyses.

## Results and Discussion

Figure 1 A), B) and C) shows plots of the kinetic data obtained for the title reactions relative to two different references. Only one example for each unsaturated alcohol and reference compound combination is shown for clarity. Reasonable linear relationships were obtained in all cases and at least two experiments have been performed with each reference compound. Contributions from secondary reactions are considered negligible since the plots show good linearity with zero or near-zero intercepts and similar results are obtained using different references.

Table 1 lists the rate coefficient ratios $k_{Alcohol}/k_{Reference}$ obtained in the individual experiments at 298 K for each unsaturated alcohol and reference compound combination. The errors given for the $k_{Alcohol}/k_{Reference}$ ratios are the 2σ statistical errors from the linear regression fits to the plots. The measurements were made relative to the reaction of OH with isobutene and (*E*)-2-butene.

$$OH + (CH_3)_2C{=}CH_2 \rightarrow \text{Products} \quad (7)$$

$$OH + CH_3CH{=}CH_2CH_3 \rightarrow \text{Products} \quad (8)$$

The rate coefficients $k_{Alcohol}$ for reactions (1) to (3) were put on an absolute basis using $k_7 = (5.23 \pm 0.24) \times 10^{-11}$ and $k_8 = (6.51 \pm 0.14) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for the reaction of OH with isobutene and (*E*)-2-butene, respectively.[22] The errors quoted for the individual $k_{Alcohol}$ values are twice the standard deviation arising from the least-squares fit of the straight lines, to which a contribution has been added to take into account the recommended errors associated with the reference rate coefficients for reactions (7) and (8).

As can be seen in Table 1, the rate coefficients are in good agreement, within the experimental uncertainties, obtained in different experiments and/or using the different reference compounds. Final rate coefficient for the reaction of OH radicals with each unsaturated alcohol is an average of all the individual values determined for that compound at 298 K:

$$k_1 = (1.14 \pm 0.14) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$k_2 = (1.28 \pm 0.23) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$k_3 = (1.49 \pm 0.35) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The final errors given for the averaged rate coefficients are the square root of the sum of the squares of the individual errors for each kinetic determination.

The value obtained in this work of $(1.14 \pm 0.14) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction of OH with *(E)*-3-hexen-1-ol is in excellent agreement with our previous value of $(1.20 \pm 0.20) \times 10^{-10}$ determined using the relative kinetic method and solid phase micro extraction (SPME) with GC-FID to monitor the reactants.[12]

To the best of our knowledge rate coefficients for the reactions of OH radicals with *(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol have not been reported previously in the literature making the present study the first OH radical kinetic study of these reactions.

*Comparison with structure-reactivity and rate coefficient relationships*

The reactivity of the unsaturated alcohols studied in this work can be compared with structure activity relationship (SAR) calculations. Rate coefficients for the title reactions have been calculated using the Environmental Protection Agency's rate coefficient calculation software, AOPWIN v1.9[23], which is based on the structure activity relationship (SAR) developed by Kwok and Atkinson.[24] The predicted values of $k_{Alcohol}$ for (*E*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol are 0.70, 0.64, and $0.66\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. These values are factors of 1.58, 1.98 and 2.24 lower than the respective experimental values. It is interesting to note that the discrepancy between experimental and predicted k increases as the carbon chain length of the unsaturated alcohols increases.

The rate coefficients determined for the unsaturated alcohols investigated in this study follow the trend $k_{(E)\text{-3-hexen-1-ol}} < k_{(Z)\text{-3-hepten-1-ol}} < k_{(Z)\text{-3-octen-1-ol}}$ which is not unexpected since in the alcohols there is an incremental addition of a methylene group (–$CH_2$–) on going from *(E)*-3-hexen-1-ol to *(Z)*-3-hepten-1-ol to *(Z)*-3-octen-1-ol. The addition of an –$CH_2$– group is expected to lead to an increase in the rate coefficient due to the extra contribution to the rate coefficient from H-atom abstraction from the additional –$CH_2$– group and also potentially an increase in the positive inductive effect of the alkyl group on the addition of OH to the double bond. The difference between the rate

coefficient obtained in this study for the reactions of OH with *(E)*-3-hexen-1-ol and *(Z)*-3-hepten-1-ol is $1.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ while that for OH with *(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol is $2.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. According to the SAR method of Kwok and Atkinson[24] adding a –$CH_2$– to the unsaturated alcohols should only add $1.149 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ of reactivity to the overall reaction. The observed incremental increases in OH reactivity on going from *(E)*-3-hexen-1-ol to *(Z)*-3-hepten-1-ol to *(Z)*-3-octen-1-ol are over an order of magnitude higher than that expected from addition of a –$CH_2$– group to the alkyl chain. This may possibly indicate that increased electron density donation to the double on increasing the alkyl chain length may be facilitating OH electrophilic addition to the double bond. However, these reactions are approaching the gas collision limit and uncertainties in the measurements may just be responsible for the apparent larger than expected increase in reactivity. For example, the reported OH rate coefficients for (*Z*)-2-penten-1-ol and (*E*)-2-hexen-1-ol are virtually the same (see Table 2) although in this comparison it is not known if the stereo chemistry may also have an effect on the measured rate coefficient. In summary, further precise measurements, preferably using different techniques, are necessary in order to establish whether or not the observed larger than expected increase in OH reactivity on going from *(E)*-3-hexen-1-ol to *(Z)*-3-hepten-1-ol to *(Z)*-3-octen-1-ol is real.

As suggested by several authors the rate coefficients for the tropospheric degradation of unsaturated volatile organic compounds by the major atmospheric oxidants can be related by linear correlations, i.e. the rate coefficients for OH addition to the compounds can be correlated with those of other tropospheric oxidants like $NO_3$ radicals, $O_3$ molecules and Cl atoms when the same primary reaction mechanism predominates.[29-32] In this work we propose a linear relationship that correlates, for the first time, the rate coefficients for the OH radical-initiated degradation of a wide range of different unsaturated alcohols with those of the analogous Cl-atom initiated reactions. Table 2 lists the 298 K rate coefficients for the Cl-atom and OH-radical reactions which have been used for deriving the proposed correlation. Figure 2 shows the relationship obtained by plotting the rate coefficients for the reactions of OH radicals with the unsaturated alcohols listed in Table 2 against the rate coefficients for the corresponding reactions with Cl atoms. A least-squares treatment of the data gives the following expression (with $k$ in units of cm$^3$ molecule$^{-1}$ s$^{-1}$):

$$\log k_{OH} = (0.29 \pm 0.04) \log k_{Cl} - 10.8 \qquad (9)$$

The linear correlation underpins that the reactions of OH radicals and Cl atoms with the unsaturated alcohols proceed by similar mechanisms, i.e. addition of the OH radical or Cl atom to the double bond in a primary reversible step. The adduct formed can react by subsequent fast reactions to products.[33]

This correlation can be used to make reasonably accurate estimations of the rate coefficients for the reactions of OH radicals or Cl atoms with unsaturated alcohols for which data are not available or are difficult to obtain experimentally.

*Mechanism and product distribution*

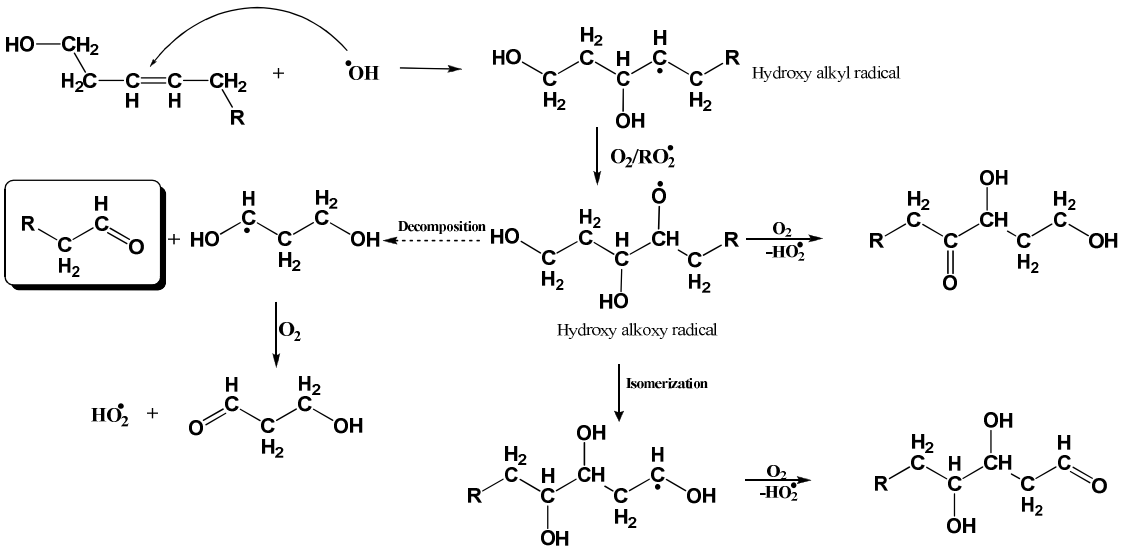
Figure 3, trace A shows the IR spectrum of a (*Z*)-3-hepten-1-ol (Z3H)/$H_2O_2$/air reaction mixture recorded before irradiation. Trace B shows to the IR spectrum acquired after UV irradiation and subtraction of residual absorptions due to Z3H. Figure 3, trace C, shows a reference spectra of butanal and trace D shows the residual spectrum obtained after subtraction of butanal from the spectrum in trace B. The absorption from $CO_2$ has been removed in traces B and C for clarity since the band was saturated and no information could be obtained from it. Butanal has been identified as a reaction product (Figure 3 trace B) based on the similarity of many of the absorption bands in the product spectrum with those of a butanal reference spectrum (Figure 3, trace C).

As can be seen in trace D even after subtraction of butanal strong absorptions still remain in the 3000-2700 $cm^{-1}$ C-H stretching region indicating that other products with a fairly long carbon skeleton are present. The rise in the spectrum baseline above 3000 $cm^{-1}$ is typical for the formation of substantial levels of secondary organic aerosol in the reaction system. According to the mechanism shown in Scheme 1, decomposition of the alkoxy radical produced after addition of OH to the carbon of the double bond closest to the OH group in (*Z*)-3-hepten-1-ol , apart from producing butanal will also lead to the formation of 3-hydroxypropanal as co-product. In fact this will be the case for all three of the unsaturated alcohols. This compound is unfortunately not readily available commercially so no direct comparison could be made with the residual product spectrum. However, the C-O stretching vibration of alcohols occurs between 1000 and 1150 $cm^{-1}$ with those for primary, secondary and tertiary alcohols occurring within fairly narrow ranges.[43] The product spectrum for (*Z*)-3-hepten-1-ol, trace D in Figure 3, shows a strong absorption centered around 1069 $cm^{-1}$ which would support the presence of a primary alcohol. Absorptions from secondary and tertiary alcohols would be expected near 1100 and 1150 $cm^{-1}$, respectively. We interpret the presence of the band at around 1069 $cm^{-1}$ as credible evidence for the formation of 3-hydroxypropanal in the reaction of OH with (*Z*)-3-hepten-1-ol. The band centered around 1069 $cm^{-1}$ is quite broad suggesting that more than one compound with an OH functionality is contributing to the band. The residual product spectrum (Figure 3 trace D) also shows the presence of different carbonyl groups the strongest of which is centered around 1730 $cm^{-1}$ and more characteristic of an aldehydic carbonyl than a ketone carbonyl group.

In analogous spectral analyses, characteristic bands of propanal and pentanal have been detected in the product spectra resulting from the reactions of OH with *(E)*-3-hexen-1-ol and *(Z)*-3-octen-1-ol, respectively. The residual product spectra from *(E)*-3-hexen-1-ol and *(Z)*-3-octen-1-ol also showed strong absorptions around 1725 and 1050 $cm^{-1}$, and the presence of an aldehydic carbonyl absorption which again supports the formation of 3-hydroxypropanal and other OH-containing products in the reaction systems.

Plots of the concentrations of aldehydes formed against reacted alcohol give molar formation yields of (37 ± 7) % for propanal and (33 ± 3) % for butanal formation in the reactions of OH with (*E*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol, respectively, in the absence of $NO_x$. The yields have been corrected for secondary consumption by OH using the method outlined in Tuazon et al.[40] Exemplary plots for (*E*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol are shown in the Supplementary Information (SI), i.e. Figures S1 and S2, respectively.

The unsaturated alcohols, like other unsaturated VOCs, react mainly by OH radical addition to the double bond (more than 90%)[9], leading to the formation of two ß-hydroxyalkyl radicals. As in the troposphere, under the present experimental conditions the ß-hydroxyalkyl radicals will add molecular $O_2$ [34] to form peroxy radicals. Under the $NO_x$-free conditions of the present study, the peroxy radicals will react further via peroxy self-reactions producing to a large extent alkoxy radicals. However, hydroperoxy and multifunctional products can be formed by molecular channels.[36] The alkoxy radicals formed can decompose, isomerize or react with $O_2$.[6,14] The potential reactions of the $RCH_2CH(O^{\cdot})CH(OH)CH_2CH_2OH$ radicals and also the reaction sequence described above are shown in the generalized Scheme 1. The decomposition reaction of the $RCH_2CH(O^{\cdot})CH(OH)CH_2CH_2OH$ radicals, indicated by the dashed line in Scheme 1, will lead to the formation of aldehydes together with 3-hydroxy-aldehydes as co-products.




**Scheme 1.** Simplified reaction mechanism for the addition channel in the OH-radical initiated oxidation of the unsaturated alcohols studied in this work (in the absence of $NO_x$), where R= $-CH_3$, $-CH_2-CH_3$, or $-CH_2-CH_2-CH_3$.

Previous products studies on the OH-radical initiated degradation of unsaturated alcohols show a higher contribution of the decomposition channel in presence of $NO_x$ as observed in this study in the absence of NOx.[6] For example, propanal has been observed with a yield of (75 ± 7) % in

a study of the OH-radical initiated degradation of (*Z*)-3-hexen-1-ol performed in the presence of $NO_x$.[37] This result contrasts sharply with the propanal yield of (37 ± 7) % obtained in this work under $NO_x$- free conditions for the reaction of OH with (*E*)-3-hexen-1-ol. Assuming that both isomers, (*Z*)-3-hexen-1-ol and (*E*)-3-hexen-1-ol react via similar reaction pathways[37], the above observations suggest that the level of $NO_x$ is a critical parameter in determining the relative contributions of the reaction channels in the oxidation of the unsaturated alcohols as has been observed for other oxygenated unsaturated compounds.[38,39]

It is known that $RO_2$ + $RO_2$/$HO_2$ reactions will affect the aldehyde yield through formation of hydroperoxides and other molecular products[42] which will lead to a reduction in the aldehyde yield and this could explain the differences discussed above. However, the large difference in the aldehyde yields we observe in the absence of NOx compared to those obtained in the presence of NOx can not be attributed solely to the formation of hydroperoxides in the reaction systems. To account for the large difference in aldehyde yields substantial amounts of hydroperoxides would have to be formed which we see no evidence for in the infrared product spectra. This leads us to believe that other factors are also playing a role. It is quite probable that the 1,2-hydroxyalkoxy radicals formed after the reaction of the 1,2-hydroxyperoxy radicals with NO will be energetically activated, a situation that will favor decomposition of the hydroxyalkoxy radicals to form the aldehyde. On the contrary, the 1,2-hydroxyalkoxy radicals formed in cross-peroxy radical reactions possess little or no activation energy and reactions of this radical with $O_2$ or other molecular channels become effective. This fact is supported by previous reports in literature of chemical activation effects in atmospheric reactions of different $RO^{\bullet}$ radicals. [40,41]

This work represents the first product study on the reaction of OH radicals with (*E*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol in the absence of $NO_x$. The product distribution under these conditions is significantly different to that obtained in the presence of $NO_x$ suggesting the necessity for further studies taking into account different atmospheric scenarios with varying $NO_x$ levels.

*Atmospheric implications*

Once in the atmosphere, a volatile organic compound is subjected to different removal processes including photolysis, homogeneous and heterogeneous reactions and wet and dry deposition.

The residence times of the alcohols in the atmosphere with respect to reaction OH radicals can be estimated using the rate coefficients obtained in this study and compared with those for their removal by other tropospheric oxidants, e.g. Cl atoms, $NO_3$ radicals and $O_3$ molecules.

The tropospheric lifetime of a volatile organic compound ($\tau$) is defined as the reciprocal of the sum of loss rates of each removal process. Thus, the tropospheric lifetime due to homogeneous reactions with OH, $NO_3$, $O_3$ and Cl are given by $\tau_x = 1/k_x[X]$ with X = OH, $NO_3$, $O_3$ and Cl, where $k_x$ is the rate

coefficient for the reaction of the oxidant X with the unsaturated alcohol and [X] is the typical atmospheric concentration of the oxidant.

The estimated tropospheric lifetimes at room temperature of the unsaturated alcohols with the tropospheric oxidants OH, $NO_3$, $O_3$ and Cl are listed in Table 3. The estimations have been made using the following rate coefficients: $k_{OH}$= 1.14 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (this work); $k_{Cl}$= 3.42 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ [20], $k_{NO3}$ = 1.56 × $10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ [13] and $k_{O3}$= 5.83 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ [44] for (*E*)-3-hexen-1-ol; $k_{OH}$= 1.28 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (this work); $k_{Cl}$ = 3.80 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ [20] for *(Z)*-3-hepten-1-ol; $k_{OH}$= 1.49 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (this work) $k_{Cl}$ = 4.13 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ [20] for *(Z)*-3-octen-1-ol.

The following typical atmospheric concentrations were used in the estimations of $\tau_x$: a 12 h daylight average OH concentration of [OH] = 2 × $10^6$ molecule $cm^{-3}$ [45], a 12 h night-time average $NO_3$ concentration of [$NO_3$] = 5 × $10^8$ molecule $cm^{-3}$ [46], a 24 h average $O_3$ concentration of 7 × $10^{11}$ molecule $cm^{-3}$ [47,] and an average of chlorine atoms concentration in marine boundary layer, coastal areas and/or some urban regions of [Cl] = 1 × $10^4$ molecule $cm^{-3}$.[48-50]

Rate data is only available for the reactions of $O_3$ and $NO_3$ with (*E*)-3-hexen-1-ol, however, those for the respective reactions with (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol are expected to be similar or slightly higher.

As Table 3 shows, the unsaturated alcohols studied in this work are rapidly removed by OH radicals in less than 2 h during the day, while during the night, the $NO_3$ reaction will govern the degradation chemistry. On the other hand, in areas with high ozone concentrations (as high as 5 × $10^{12}$ molecules $cm^{-3}$) the reaction with $O_3$ can compete with OH removal. However, due to the low Cl atom concentration in the troposphere the contribution of chlorine chemistry is negligible.

The products formed by the OH-initiated oxidation of the unsaturated alcohols studied in this work will be to a large extent aldehydic in nature and can contribute through further oxidation to the formation of ozone, long-lived nitrogen containing compounds (PANs) and other oxidants in the troposphere. The work highlights the need for product studies to performed using atmospherically relevant levels of NOx in the reaction systems.

Recent studies have shown the formation of secondary organic aerosols (SOA) in the OH-radical degradation of unsaturated alcohols with OH radicals[51] which is also supported by the observations of the present study, however more detailed laboratory studies on SOA formation for these reactions studied are needed.

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## Supporting Information Available

Yield plots for the reaction of OH radicals with (*E*)-3-hexen-1-ol (S3) and (*Z*)-3-hepten-1-ol (S1 and S2) in the absence of $NO_x$. Infrared spectra obtained for (E)-3-hexen-1-ol /$H_2O_2$/air reaction (S3).This information is available free of charge via the Internet at http://pubs.acs.org.

## Literature Cited

(1) Fall, R.; Karl, T.; Hansel, A.; Jordan, A.; Lindinger, W. Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry. *J. Geophys. Res*. **1999**, *104*, 15, 963–974.

(2) Buttery, R. G.; Ling, L. C. Volatile components of tomato fruit and plant parts: Relationship and biogenesis. Bioactive Volatile Compounds from Plants. ACS Symposium Series 525. American Chemical Society, Washington DC **1993**, *3*, 23–34.

(3) Heiden, A.C.; Kobel, K.; Langebartels, C.; Schuh-Thomas, G.; Wildt, J. Emissions of Oxygenated Volatile Organic Compounds from Plants Part I: Emissions from Lipoxygenase Activity. *J. Atmos. Chem.* **2003**, *45*, 143–172.

(4) Dalai, A.; Schoenau, G.; Das, D.; Adapa, P. Volatile Organic Compounds emitted during High-temperature Alfalfa Drying. *Biosyst. Eng*. **2006**, *94*, 57–66.

(5) Cilek, J.E.; Ikediobi, C.O.; Hallmon, C.F.; Johnson, R.; Onyeozili, E.N.; Farah, S.M.; Mazu, T.; Latinwo, L.M.; Ayuk-Takem, L.; Berniers, U.R. Semi–field evaluation of several novel alkenol analogs of 1-octen-3-ol as attractants to adult *Aedes Albopictus* and *Culex Quinquefasciatus*. *J. Am. Mosquito Control Assoc*. **2011**, *27*, 256–262.

(6) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103*, 4605–4638.

(7) Mellouki, A.; Le Bras, G.; Sidebottom, H. Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase. *Chem. Rev*. **2003**, *103*, 5077–5096.

(8) Calvert, J. G.; Mellouki, A.; Orlando, J. J.; Pilling, M. J.; Wallington, T. J. The mechanism of atmospheric oxidation of the oxygenates. Oxford University Press: New York, **2011**.

(9) Atkinson, R.; Arey, J.; Aschmann S. M.; Corchnoy, S. B.; Shu, Y. Rate constants for the gas-phase reactions of cis-3-hexen-1-ol, cis-3-hexenylacetate, trans-2-hexenal, and linalool with OH and $NO_3$ radicals and $O_3$ at 296 ± 2 K, and OH radical formation yields from the $O_3$ reactions. *Int. J. Chem. Kin.* **1995**, *27*, 941-955.

(10) Jimenez, E.; Lanza, B.; Antiñolo, M.; Albaladejo, J. Photooxidation of leaf-wound oxygenated compounds, 1-penten-3-ol, (Z)-3-hexen-1-ol, and 1-penten-3-one, initiated by OH radicals and sunlight. *Environ. Sci. Technol*. **2009**, *43*, 1831–1837.

(11) Davis M. E.; Burkholder, J. B. Rate coefficients for the gas-phase reaction of OH with (Z)-3-hexen-1-ol, 1-penten-3-ol, (*E*)-2-penten-1-ol, and (*E*)-2-hexen-1-ol between 243 and 404K. *Atmos. Chem. Phys.* **2011**, *11*, 2377–2405.

(12) Gibilisco, R.G.; Santiago, A.N.; Teruel, M.A. OH-initiated degradation of a series of hexenols in the troposphere. Rate coefficients at 298 K and 1 atm. *Atmos. Environ*. **2013**, *77*, 358-364.

(13) Pfrang C.; Martin R. S.; Canosa-Mas C. E.; Wayne R. P. Gas-phase reactions of $NO_3$ and $N_2O_5$ with *(Z)*-hex-4-en-1-ol, *(Z)*-hex-3-en-1-ol ('leaf alcohol'), (*E*)-hex-3-en-1-ol, *(Z)*-hex-2-en-1-ol and (*E*)-hex-2-en-1-ol. *Phys. Chem. Chem. Phys*. **2006**, *8*, 315-320.

(14) Grosjean, D.; Williams, E. L. II.; Grosjean, E. A biogenic precursor of peroxypropionyl nitrate: Atmospheric oxidation of *cis-3-hexen-l-ol. Environ. Sci. Technol*. **1993**, *27*, 979-981.

(15) Rodríguez, A.; Rodríguez, D.; Garzón, A.; Soto, A.; Aranda, A.; Notario, A. Kinetics and mechanism of the atmospheric reactions of atomic chlorine with 1-penten-3-ol and (*Z*)-2-penten-1-ol: an experimental and theoretical study. *Phys. Chem. Chem. Phys*. **2010**, *12*, 12245-12258.

(16) Rodríguez, A.; Rodríguez, D.; Soto, A.; Notario, A.; Aranda, A.; Díaz-de-Mera, Y.; Bravo, I. Relative rate measurements of reactions of unsaturated alcohols with atomic chlorine as a function of temperature. *Atmos. Environ*. **2007**, *41*, 4693–4702.

(17) Rodríguez, D.; Rodríguez, A.; Soto, A.; Aranda, A.; Díaz-de-Mera, Y., Notario, A. Kinetics of the reactions of Cl atoms with 2-buten-1-ol, 2-methyl-2-propen-1-ol, and 3-methyl-2-buten-1-ol as a function of temperature. *J. Atmos. Chem*. **2008**, *59*, 187-197.

(18) Rodríguez, D.; Rodríguez, A.; Soto, A.; Aranda, A.; Díaz-de-Mera, Y.; Notario, A. Response on the comment on "Kinetics of the reactions of Cl atoms with 2-buten-1-ol, 2-methyl-2-propen-1-ol, and 3-methyl-2-buten-1-ol as a function of temperature". *J. Atmos. Chem*. **2008**, *59*, 187-197.

(19) Liang, P.; Mua, Y.J.; Daële, V.; Mellouki, A. Kinetic studies of Cl reactions with 3-buten-1-ol and 2-buten-1-ol over the temperature range 298–363 K. *Chem. Phys. Lett.* **2011**, *502*, 154–158.

(20) Gibilisco R. G.; Bejan I.; Barnes I.; Wiesen P.; Teruel M. A. Rate coefficients at 298 K and 1 atm for the tropospheric degradation of a series of C6, C7 and C8 biogenic unsaturated alcohols initiated by Cl atoms. *Atmos. Environ*. **2014**, *94*, 564-572.

(21) Barnes, I.; Becker, K.; Zhu, T. Near. UV absorption spectra and photolysis products of difunctional organic nitrates: Possible importance as $NO_x$ reservoirs. *J. Atmos. Chem*. **1993**, *17*, 353-373.

(22) Atkinson, R.; Aschmann S. M. Rate constants for the reaction of OH radicals with a series of alkenes and dialkenes at 295 ± 1 K. *Int. J. Chem. Kinet*. **1984**, *16,* 1175–1186.

(23) US Environmental Protection Agency. AOPWIN v1.91, http://www.epa.gov/opptintr/exposure/ docs/episuite.htm: Washington D.C, **2000**.

(24) Kwok, E.; Atkinson, R. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update. *Atmos. Environ*. **1995**, *29*, 1685-1695.

(25) Papagni C.; Arey J.; Atkinson R. Rate constants for the gas-phase reactions of OH radicals with a series of unsaturated alcohols. *Int. J. Chem. Kin*. **2001**, *33,* 142–147.

(26) Imamura, T.; Lida, Y.; Obi, K.; Nagatani, I.; Nacagawa, K.; Patroescu-Klotz, I.; Hatakeyama, S. Rate Coefficients for the Gas-Phase Reactions of OH Radicals with Methylbutenols at 298 K. *Int. J. Chem. Kin*. **2004**, *36*, 379-385.

(27) Orlando J. J.; Tyndall G. S.; Ceazan N. Rate Coefficients and Product Yields from Reaction of OH with 1-Penten-3-ol, (Z)-2-Penten-1-ol, and Allyl Alcohol (2-Propen-1-ol). *J. Phys. Chem. A.* **2001**, *105*, 3564–3569.

(28) Cometto, P. M.; Dalmasso, P. R.; Taccone, R. A.; Lane, S. I.; Oussar, F., Daele, V.; Mellouki, A.; Le Bras, G. Rate Coefficients for the Reaction of OH with a Series of Unsaturated Alcohols between 263 and 371 K. *J. Phys. Chem. A*. **2008**, *19*, 4444–4450.

(29) Atkinson, R. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. *J. Phys. Chem*. **1997**, *26*, 215–290.

(30) Wayne, R.P.; Barnes, I.; Biggs, P.; Burrows, J.P.; Canosa – Mas, C.E.; Hjorth, J.; Le Bras, G.; Moortgat, G.K.; Pernon, D.; Poulet, G.; Restelli, G.; Sidebottom, H. The nitrate radical: physics, chemistry, and the atmosphere. *Atmos. Environ. Part A*. **1991**, *25*, 1–203.

(31) Baumgartner, M.T.; Teruel, M.A.; Taccone, R.A.; Lane, S.I. Theoretical study of the relative reactivity of chloroethenes with atmospheric oxidants OH, $NO_3$, $O(^3P)$, $Cl(^2P)$ and $Br(^2P)$. *Phys. Chem. Chem. Phys*. **2002**, *4*, 1028–1032.

(32) Blanco M. B.; Bejan I.; Barnes I.; Wiesen P.; Teruel M. A. Temperature-dependent rate coefficients for the reactions of Cl atoms with methyl methacrylate, methyl acrylate and butyl methacrylate at atmospheric pressure. *Atmos. Environ*. **2009**, *43*, 5996–6002.

(33) Calvert, J.G.; Atkinson, R.; Kerr, J.A.; Madronich, S.; Moortgat, G.K.; Wallington, T.J.; Yarwood, G. Mechanisms of Atmospheric Oxidation of the Alkanes. Oxford University Press: New York, USA, **2000**.

(34) Atkinson, R. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem*. **1994**, *2*, 1-216.

(35) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. Organic peroxy radicals: kinetics, spectroscopy and tropospheric chemistry. *Atmos. Environ*. **1992**, *26A*, 1805−1964.

(36) Tuazón, E.C.; Mac Leod, H.; Atkinson, R.; Carter W.P.L. α-Dicarbonyl yields from $NO_x$-air photooxidations of a series of aromatic hydrocarbons in air. *Environ. Sci. Technol.* **1986**, *20*, 383-387.

(37) Aschmann, S.; Yonghui, S.; Arey J.; Atkinson, R. Products of the gas-phase reactions of Cis-3-hexen-1-ol with OH radicals and $O_3$. *Atmos. Environ*. **1997**, *31*, 3551-3560.

(38) Blanco M. B.; Bejan I.; Barnes I.; Wiesen P.; Teruel M. A. Products and mechanism of the reactions of OH radicals and Cl atoms with methyl methacrylate ($CH_2$=$C(CH_3)C(O)OCH_3$) in the Presence of $NO_x$. *Env. Sci. Technol*. **2014**, *48*, 1692−1699.

(39) Blanco M. B.; Bejan I.; Barnes I.; Wiesen P.; Teruel M. A. Atmospheric Oxidation of Vinyl acetate and Allyl acetate: Product Distribution and Mechanisms of the OH-Initiated Degradation in the Presence and the Absence of NOx. *Env. Sci. Technol*. **2012**, *46*, 8817− 8825.

(40) Hurley, M.D; Wallington, T.J.; Bjarrum, M.; Javadi, M.S.; Nielsen, O.J. Atmospheric chemistry of 3-pentanol: kinetics, mechanisms, and products of Cl atom and OH radical initiated oxidation in the presence and absence of NOx. *J. Phys. Chem. A*. **2008**, *112*, 8053-8060.

(41) Hurley, M.D.; Wallington, T.J.; Laursen, L.; Javadi, M.S.; Nielsen, O.J., Yamanaka, T.; Kawasaki, M. Atmospheric chemistry of *n*-butanol: kinetics, mechanisms, and products of Cl atom and OH radical initiated oxidation in the presence and absence of NOx. *J. Phys. Chem. A*. **2009**, *113*, 7011-7020.

(42) Navarro M. A.; Dusanter, S.; Hites R A., Stevens P. S. Radical Dependence of the Yields of Methacrolein and Methyl Vinyl Ketone from the OH-Initiated Oxidation of Isoprene under NOx-Free Conditions. *Environ. Sci. Technol*. **2011**, *45*, 923–929

(43) Bellamy, L. J. The infrared spectra of complex molecules, John Wiley and Sons, Inc.: New York, **1978**.

(44) Gibilisco R. G., Bejan I., Barnes I., Wiesen P., Teruel M. A. FTIR gas kinetic study of the reactions of ozone with a series of hexenols at atmospheric pressure and 298 K. *Chem. Phys. Lett*. **2015**, *618*, 114-118.

(45) Hein, R.; Crutzen, P. J.; Heimann, M. An inverse behaviour approach to investigate the global atmospheric methane cycle. *Glob. Biogeochem. Cycles*. **1997**, *11*, 43–76.

(46) Shu, Y., Atkinson, R. Atmospheric lifetimes and fates of a series of sesquiterpenes. *J. Geophys. Res.*, **1995**, *100*, 7275–7281.

(47) Logan J. A. Tropospheric ozone: Seasonal behaviour, trends, and anthropogenic influence. *J. Geophys. Res*. **1985**, *90*, 463–482.

(48) Wingenter, O.W.; Kubo, M.K.; Blake, N.J.; Smith, T.W.; Blake, D.R.; Rowland, F.S. Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights. *J. Geophys. Res.* **1996**, *101*, 4331–4340.

(49) Wingenter O.W.; Sive B. C.; Blake N. G.; Blake D. R.; Rowland, F.S. Atomic Chlorine concentrations derived from ethane and hydroxyl measurements over the equatorial Pacific ocean: Implications for dimethyl sulphide and bromide monoxide. *J. Geophys. Res.* **2005**, *110*, D20308.

(50) Tanaka P. L.; Riemer D. D.; Chang S.; Yarwood G.; Mc Donald-Buller E. C.; Apel E. C.; Orlando J. J.; Silva P. J.; Jimenez J. L.; Canagaratna, M. R..; Neece J. D..; Mullins C. B.; Allen D. T. Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. Atmos. Environ. **2003**, *37*, 1393-1400

(51) Jaoui M.; Kleindienst T. E.; Offenberg J. H.; Lewandowski M.; Lonneman W. A. SOA formation from the atmospheric oxidation of 2-methyl-3-buten-2-ol and its implications for PM2.5. *Atmos. Chem. Phys*. **2012**, *12*, 2173–2188.

## Figure Captions

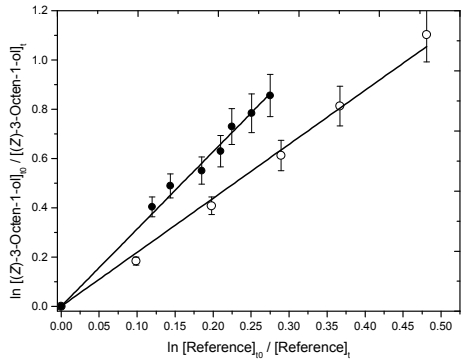
**FIGURE 1.** A) Plot of the kinetic data for the reaction of *(Z)*-3-octen-1-ol with OH radicals using isobutene (●) and (*E*)-2-butene (○) as reference hydrocarbons. B) Plot of the kinetic data for the reaction of *(E)*-3-hexen-1-ol, with OH radicals using isobutene and C) Plot of the kinetic data for the reaction of *(Z)*-3-hepten-1-ol with OH radicals using isobutene (●) and (*E*)-2-butene (○) as reference hydrocarbons.

**FIGURE 2**. Linear free energy plot of log $k_{OH}$ against log $k_{Cl}$ at room temperature for a series of unsaturated alcohols (numbers: 1 (3-buten-2-ol); 2 (2-methyl-3-buten-2-ol); 3 (1-penten-3-ol); 4 (2-methyl-2-propen-1-ol); 5 ((*Z*)-3-hexen-1-ol); 6 (*(Z)*-2-penten-1-ol); 7 (2-buten-1-ol); 8 (*(E)*-2-hexen-1-ol) and 11 (3-methyl-2-buten-1-ol) including the room temperature rate coefficients for the reactions obtained in this work (open triangles, numbers: 9 (*(E)*-3-hexen-1-ol); 10 (*(Z)*-3-hepten-1-ol) and 12 (*(Z)*-3-octen-1-ol)).

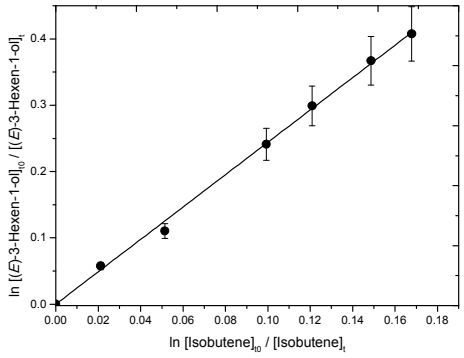
**FIGURE 3**. Trace A shows the infrared spectrum of a *(Z)*-$CH_2(OH)CH_2CH{=}CHCH_2CH_2CH_3/H_2O_2$/air reaction mixture before irradiation and trace B shows the IR spectrum after irradiation and subtraction of residual Z3H. Trace C shows a reference spectrum of butanal and D shows the residual product spectrum obtained after subtraction of features due to butanal from the spectrum in trace B.

**FIGURE 1**

**A)**


ln [(Z)-3-Octen-1-ol]t0 / [(Z)-3-Octen-1-ol]t
ln [Reference]t0 / [Reference]t

**B)**


ln [(E)-3-Hexen-1-ol]t0 / [(E)-3-Hexen-1-ol]t
ln [Isobutene]t0 / [Isobutene]t

**C)**

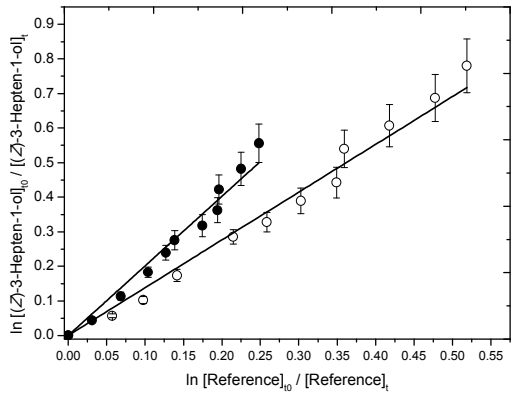

ln [(Z)-3-Hepten-1-ol]t0 / [(Z)-3-Hepten-1-ol]t
ln [Reference]t0 / [Reference]t

**FIGURE 2**

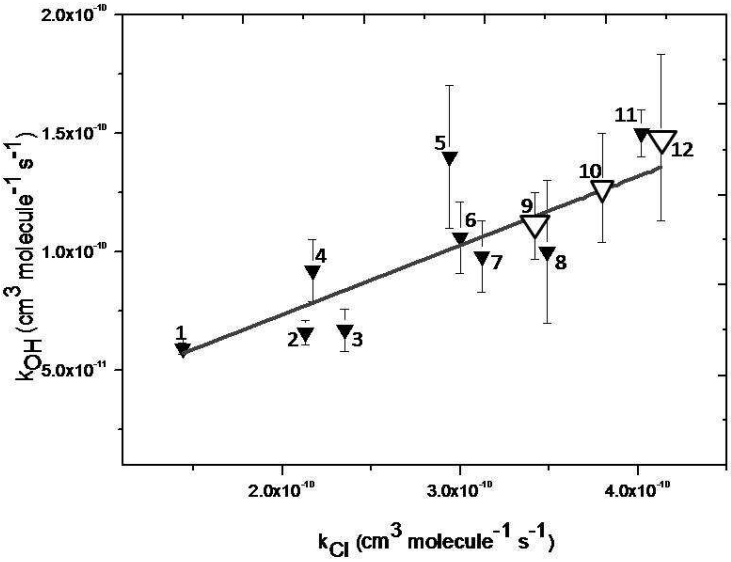

2.0x10⁻¹⁰
1.5x10⁻¹⁰
1.0x10⁻¹⁰
5.0x10⁻¹¹
k_OH (cm³ molecule⁻¹ s⁻¹)
2.0x10⁻¹⁰
3.0x10⁻¹⁰
4.0x10⁻¹⁰
k_Cl (cm³ molecule⁻¹ s⁻¹)
1
2
3
4
5
6
7
8
9
10
11
12

**FIGURE 3**

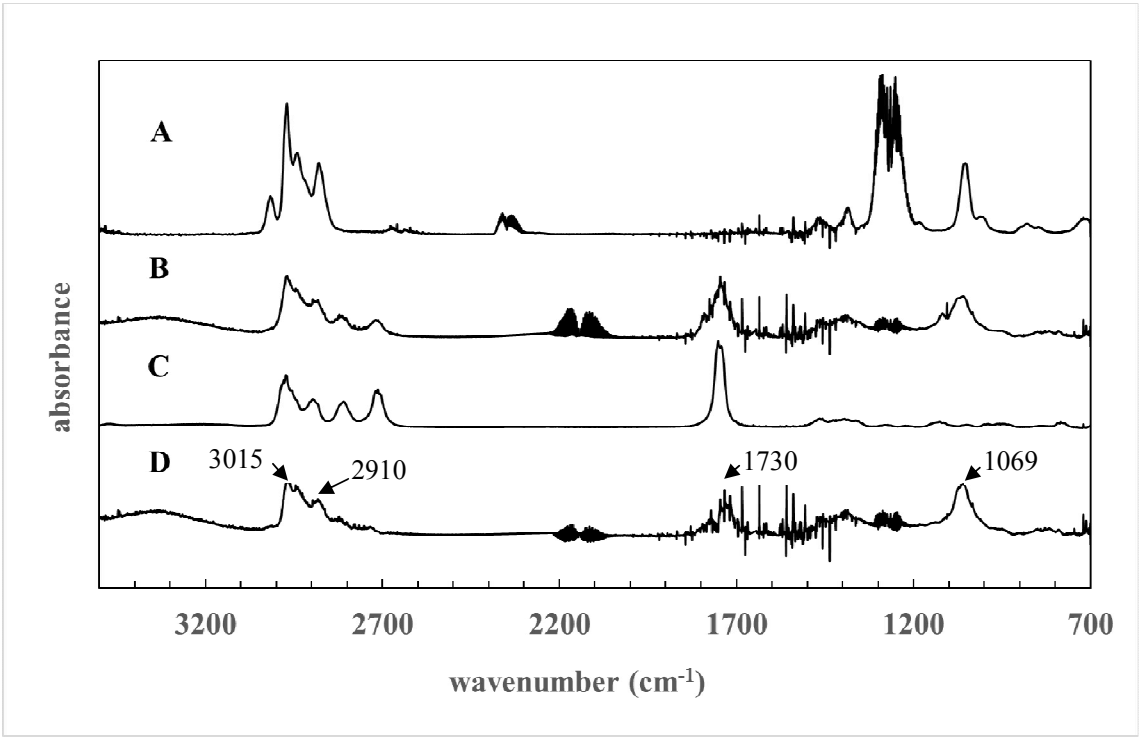

A
B
C
D
absorbance
3015
2910
1730
1069
3200
2700
2200
1700
1200
700
wavenumber (cm-1)

**TABLE 1:** Rate coefficient ratios $k_{Alcohol}/k_{Reference}$ and rate coefficients for the reactions of OH radicals with *(E)*-3-hexen-1-ol, *(Z)*-3-hepten-1-ol and *(Z)*-3-octen-1-ol at (298 ± 3) K in 1 atm of air.

| Unsaturated Alcohol | Reference | $k_{Alcohol}/k_{Reference}$ | $k_{Alcohol+OH}$ ($10^{-10}$cm$^3$ molecule$^{-1}$s$^{-1}$) |
|---|---|---|---|
| *(E)*-3-hexen-1-ol | $C_4H_8$ | 2.02±0.10 | 1.06 ± 0.10 |
| | $C_4H_8$ | 2.33±0.11 | 1.22 ± 0.10 |
| | **Average** | | **1.14 ± 0.14** |
| (*Z*)-3-hepten-1-ol | $CH_3CH=CHCH_3$ | 1.88±0.10 | 1.22 ± 0.10 |
| | $CH_3CH=CHCH_3$ | 2.14±0.12 | 1.39 ± 0.11 |
| | $C_4H_8$ | 2.51±0.16 | 1.31 ± 0.14 |
| | $C_4H_8$ | 2.29±0.10 | 1.20 ± 0.10 |
| | **Average** | | **1.28 ± 0.23** |
| (*Z*)-3-Octen-1-ol | $CH_3CH=CHCH_3$ | 2.48±0.34 | 1.61 ± 0.26 |
| | $CH_3CH=CHCH_3$ | 2.34±0.11 | 1.52 ± 0.10 |
| | $C_4H_8$ | 2.67±0.18 | 1.40 ± 0.16 |
| | $C_4H_8$ | 2.72±0.15 | 1.42 ± 0.14 |
| | **Average** | | **1.49 ± 0.35** |

**TABLE 2:** Rate coefficients of the reactions of Cl atoms and OH radicals with unsaturated alcohols.

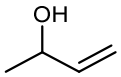
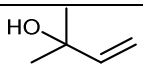
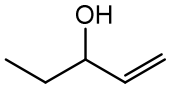
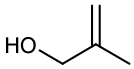
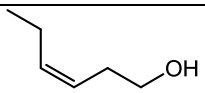
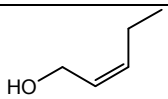
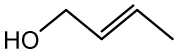
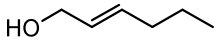
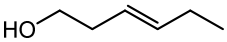
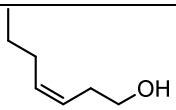
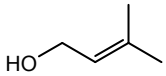
| | Unsaturated Alcohol | $k_{Cl} \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $k_{OH} \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 1 |  3-buten-2-ol | 1.44 ± 0.17 [16] | 0.59 ± 0.02 [25] |
| 2 |  2-methyl-3-buten-2-ol | 2.13 ± 0.19 [16] | 0.66 ± 0.05 [26] |
| 3 |  1-penten-3-ol | 2.35 ± 0.31 [15] | 0.67 ± 0.09 [27] |
| 4 |  2-methyl-2-propen-1-ol | 2.17 ± 0.39 [17,18] | 0.92 ± 0.13 [28] |
| 5 |  (Z)-3-hexen-1-ol | 2.94 ± 0.72 [20] | 1.4 ± 0.3 [12] |
| 6 |  (Z)-2-penten-1-ol | 3.00 ± 0.49 [15] | 1.06 ± 0.15 [27] |
| 7 |  2-buten-1-ol | 3.12 ± 0.64 [17,18] | 0.98 ± 0.15 [28] |
| 8 |  (E)-2-hexen-1-ol | 3.49 ± 0.82 [20] | 1.0 ± 0.3 [12] |
| 9 |  (E)-3-hexen-1-ol | 3.92 ± 0.79 [20] | 1.14 ± 0.14 (this work) |
| 10 |  (z)-3-hepten-1-ol | 3.80 ± 0.86 [20] | 1.28 ± 0.23 (this work) |
| 11 |  3-methyl-2-buten-1-ol | 4.02 ± 0.56 [17,18] | 1.50 ± 0.10 [26] |

**TABLE 3:** Estimated atmospheric lifetimes for the reactions of the unsaturated alcohols studied in this work with OH and $NO_3$ radicals, $O_3$ and Cl atoms.

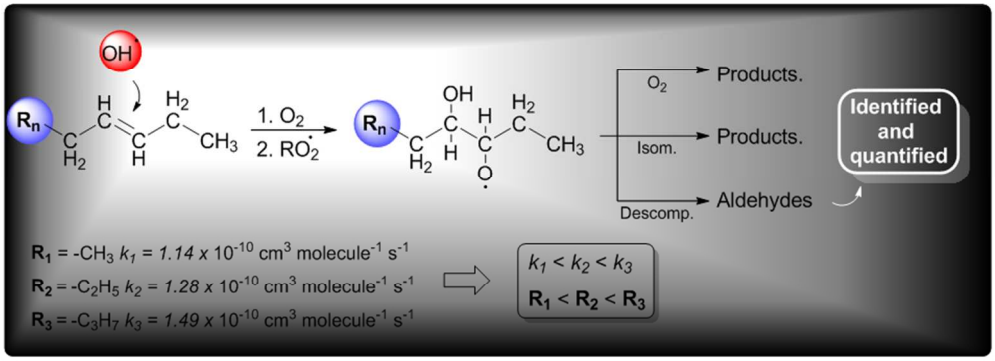
| Alcohol | $\tau_{OH}$ (hours) | $\tau_{NO3}$ (hours) | $\tau_{O3}$ (hours) | $\tau_{Cl}$ (hours) |
|---|---|---|---|---|
| *(E)*-3-hexen-1-ol | 1.25 | 1.3 | 6.9 | 81 |
| *(Z)*-3-hepten-1-ol | 1.09 | - | - | 73 |
| *(Z)*-3-octen-1-ol | 0.94 | - | - | 67 |

[OH] = $2 \times 10^6$ molecule $cm^{-3}$ [45]

$[NO_3] = 5 \times 10^8$ molecule $cm^{-3}$ [46]

$[O_3] = 7 \times 10^{11}$ molecule $cm^{-3}$ [47]

[Cl] = $1 \times 10^4$ molecule $cm^{-3}$. [48-50]




TOC graphical abstract
254x190mm (96 x 96 DPI)