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OH-initiated degradation of a series of hexenols in the troposphere. Rate coefficients at 298 K and 1 atm

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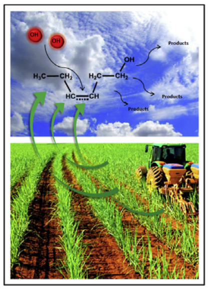
HIGHLIGHTS

- First reactivity study of OH-atmospheric oxidation of unsaturated hexenols.
- Relative kinetics and products identification by SPME-GC-FID-MS at 298 K and 1 atm.
- Reactivity trends developed in terms of substitution effects.
- E_{HOMO} calculations of alcohols correlated with their rate coefficients.
- Atmospheric lifetimes of hexenols determined and possible impact assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

The kinetics of the reactions of OH radicals with three C_6 unsaturated alcohols at 298 K and atmospheric pressure were investigated using solid phase microextraction (SPME) with GC-FID detection of organic compounds. Rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}) of $k_1(OH + (E)\text{-}CH_2OHCH{=}CH(CH_2)_2CH_3) = (1.0 \pm 0.3) \times 10^{-10}$, $k_2(OH + (E)\text{-}CH_2OHCH_2CH{=}CHCH_2CH_3) = (1.2 \pm 0.2) \times 10^{-10}$ and $k_3(OH + (Z)\text{-}CH_2OHCH_2CH{=}CHCH_2CH_3) = (1.4 \pm 0.3) \times 10^{-10}$ were obtained by the relative rate method using methyl methacrylate and (*E*)-2-buten-1-ol as references. Rate coefficients were compared with previous determinations and reactivity trends were developed and rationalized in terms of the effect and position of substituents in the unsaturated alcohol. A correlation between the reactivity of unsaturated alcohols toward OH radicals and the energy of the HOMO of the unsaturated alcohol is presented.

Additionally, product identification under atmospheric conditions was performed for the first time for these unsaturated C6 alcohols by the GC–MS technique. Butanal was observed as the main degradation product of OH with (*E*)-2-hexen-1-ol, in accordance with the decomposition of the 2,3-hydroxyalcoxy radicals formed. On the basis of our kinetic measurements, tropospheric lifetimes of the studied unsaturated compounds are estimated.

1. Introduction

Volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) can be released to the air from different sources of biogenic origin or anthropogenic origin. Unsaturated

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alcohols are emitted extensively by their use as solvents in different industries or by vegetation (Graedel, 1978). Furthermore, these compounds can be produced by photooxidation of other VOCs released to the atmosphere (Heiden et al., 2003). Consequently, large amount of these organics are daily found in the air and can by degraded by physical and chemical processes. In this sense, it is necessary a detailed study of their reactivity toward the main oxidants in the troposphere as well as the products formed in these reactions to assess their impact in the air quality.

Hexenols are unsaturated alcohols released to the atmosphere mainly by vegetation. These VOCs can be found in the emission of freshly mown grass (Gardner, 1991).

(*Z*)-3-hexen-1-ol (leaf alcohol) and (*E*)-3-hexen-1-ol (leaf alcohol) can be found after wounding and during drying and pathogen attack (Heiden et al., 2003). The leaf alcohol is found also to be the main chemical from the emission of lima bean leaves (Arimura et al., 2000) and herbivory-induced emission from maize seedlings (Farag et al., 2005). (*Z*)-2-hexen-1-ol has also been reported to be released by clipped clover (Kirstine et al., 1998). (*Z*)-3-hexen-1-ol and (*E*)-3-hexen-1-ol also has been observed as VOCs of purple-skinned passion fruit (Murray et al., 1972) and freshly distilled Calvados and Cognac (Ledauphin et al., 2004). Furthermore, recent studies demonstrated the activity of the (*Z*)-3-hexen-1-ol, in combination with a volatile pheromone, such an attractor of emerald ash borer (*Agrilus planipennis*) using baited green sticky traps for the control of this plague (Ryall et al., 2012).

Although, kinetics and product studies for saturated alcohols are reported in literature (Atkinson and Arey, 2003; Mellouki et al., 2003; Calvert et al., 2011), there are a few studies for the reactions of the main tropospheric oxidants with unsaturated alcohols, mainly butenols and some few pentenols (Calvert et al., 2011). The reactivity and mechanistic information for C6 alcohols is even scant. There is a relative determination (Atkinson et al., 1995) and two pulsed laser photolysis studies of the reaction of OH radicals with (*Z*)-3-hexen-1-ol (Jimenez et al., 2009; Davis and Burkholder, 2011). The last authors also determined the rate coefficient of (*Z*)-2-hexen-1-ol in the temperature range of 243–404 K and pressures from 20 to 100 Torr. There is a low-pressure flow study for the reactions of NO_3 and N_2O_5 with a series of hexenols coupled with relative determinations using collapsible Teflon chambers at 1 atm (Pfrang et al., 2006). The authors estimated atmospheric lifetimes between 1 and 4 h, and OH radicals seems to be the main oxidant in the troposphere and during daytime.

In order to assess the environmental impact of these species, kinetic and mechanistic information on their tropospheric degradation is therefore needed.

In this work, we report rate coefficients for the reactions of OH radicals with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol:

$$(E)-CH_2OHCH=CH(CH_2)_2CH_3+OH\rightarrow \text{Products} \quad (1)$$

$$(E)-CH_2OHCH_2CH=CHCH_2CH_3+OH\rightarrow \text{Products} \quad (2)$$

$$(Z)-CH_2OHCH_2CH=CHCH_2CH_3+OH\rightarrow \text{Products} \quad (3)$$

Experiments were conducted using the relative method with different reference compounds at room temperature and atmospheric pressure. In addition, product studies using the GC–MS technique under atmospheric conditions were carried out for the first time for these unsaturated alcohols and the degradation pathways are also discussed.

Our work aims to better define the reactivity of the $RCH=CHR'$ (R and $R'=$ H, alkyl and or oxygenated substituents) compounds toward OH radicals. In this sense, the results are also discussed in terms of the substituent effects on the reactivity of the olefinic carbons and correlated with the energy of the HOMO of the hexenols.

Lifetimes of the VOCs studied in this work were calculated taking into account the experimental rate constants obtained and the averaged oxidant tropospheric concentrations.

2. Experimental

The experimental set-up consisted of an 80 L Teflon bag located in a wooden box with the internal walls covered with aluminum foil, and operated at atmospheric pressure (750 ± 10) Torr and (298 ± 1) K.

The amounts of the organic reactants measured were flushed into the bag with a stream of nitrogen. The bag was then filled to its full capacity at atmospheric pressure with nitrogen. H_2O_2 was used to generate OH radicals by its photolysis using a set of germicidal lamps:

$$H_2O_2\rightarrow 2OH \quad (4)$$

These lamps provide UV-radiation with a λ maximum around 254 nm. In the present work, typically 6 of these lamps were used to produce OH radicals and the time of photolysis varied from 2 to 5 min.

Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in nitrogen, were introduced in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Before each set of experiments, the bag was cleaned by filling it with a mixture of O_2 and N_2 photolyzed for 15–25 min using 4 germicidal lamps (Philips 30W) with a UV emission at 254 nm, to produce O_3. After this procedure, the bag was cleaned up again by repeated flushing with air and the absence of impurities was checked by gas chromatography before performing the experiments.

Gas samples were periodically removed from the Teflon bag using an SMPE technique, DVB/CAR/PDMS coated fiber was employed because it shows a good response for these compounds. The time of adsorption was 15 min at 298 K and desorption was carried out into the injector port for 2 min at 473 K.

Organic compounds were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using an HP-20M capillary column (Carbowax 20M, 25 m, 0.2 mm, 0.1 μm) held from 40 to 120 °C.

In the presence of the oxidant OH radical the alcohols studied and the references decay through the following reactions:

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

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

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

$$\ln\left\{\frac{[\text{Alcohol}]_0}{[\text{Alcohol}]_t}\right\}=\frac{k_5}{k_6}\ln\left\{\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right\} \quad (I)$$

where $[\text{Alcohol}]_0$, $[\text{Reference}]_0$, $[\text{Alcohol}]_t$ and $[\text{Reference}]_t$ are the concentrations of the alcohol and the reference compound at times $t=0$ and t, respectively, and k_5 and k_6 are the rate constants of reactions (5) and (6), respectively.

The relative rate technique relies on the assumption that the alcohol and the reference compounds are removed solely by reaction with OH radicals. To verify this assumption, mixtures of hydrogen peroxide and air with the alcohol of interest and the reference compound were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the precursor of OH (hydrogen peroxide), in the absence of UV light, was of negligible importance over the typical time periods used in this work.

Furthermore, to test for possible photolysis of the reactants used, mixtures of the alcohols in air, in the absence of hydrogen peroxide, were irradiated for 30 min using the output of all the germicidal lamps surrounding the chamber. No significant photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 59–124 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) for the unsaturated alcohols, 74–300 ppm for methyl methacrylate and (*E*)-2-buten-1-ol.

The analytical technique employed for qualitative identification of the products formed after irradiation was terminated was GC-mass spectrometry on a Shimadzu GC–MS QP 5050 spectrometer equipped with a 30 m–0.12 mm DB-5 MS column.

3. Materials

The following chemicals with purities as stated by the supplier were used without further purification: nitrogen (AGA, 99.999%), (*E*)-2-hexen-1-ol (Aldrich, 96%), (*E*)-3-hexen-1-ol (Aldrich, 97%) and (*Z*)-3-hexen-1-ol (Aldrich, 98%), methyl methacrylate (Aldrich, 99.99%), (*E*)-2-buten-1-ol (Aldrich, 96%), and H_2O_2 (Cicarelli, 60% wt).

4. Results and discussion

Relative rate coefficients for the reactions of OH radicals with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol were determined by comparing the OH reaction with the alcohols studied to that with the reference compounds from Eq. (I). A straight line was fitted to the data by the linear least-squares procedure.

The losses of (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol by OH radicals are shown with different reference compounds in Figs. 1–3. Figs. 1–3 show only one example with two references for each reaction studied.

The following compounds were used as reference reactions to determine the rate coefficients of the reactions (1)–(3):

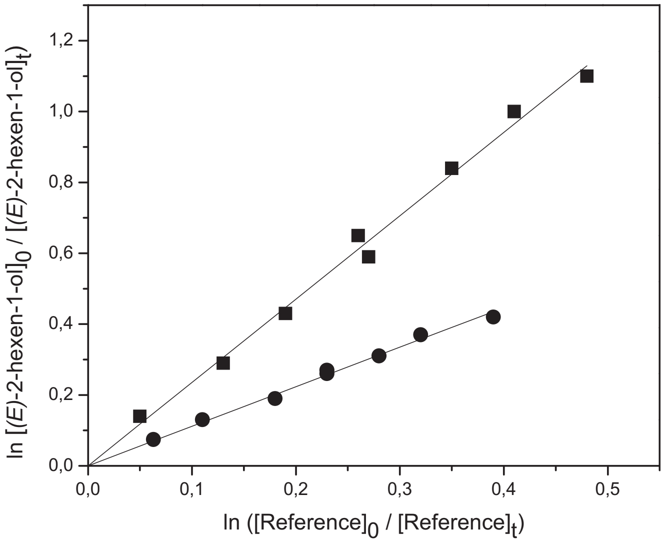


Fig. 1. Plot of the kinetic data for the reaction of (*E*)-2-hexen-1-ol with OH radicals using methyl methacrylate (■) and (*E*)-2-buten-1-ol (●) as reference hydrocarbons.

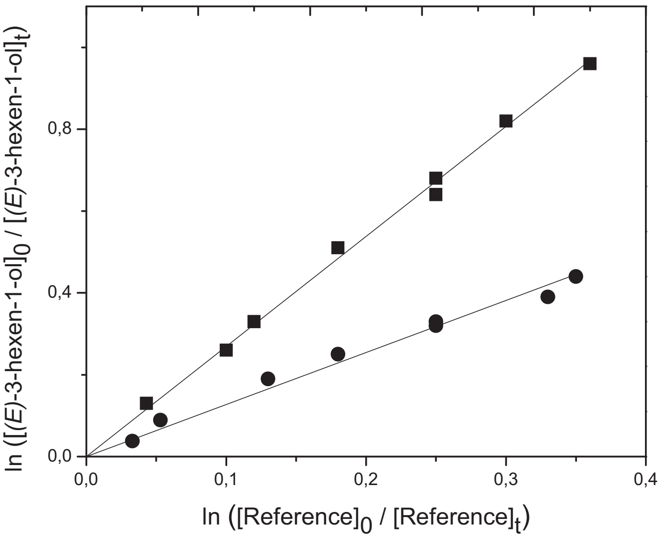


Fig. 2. Plot of the kinetic data for the reaction of (*E*)-3-hexen-1-ol, with OH radicals using methyl methacrylate (■) and (*E*)-2-buten-1-ol (●) as reference hydrocarbons.

$$OH + CH_2 = C(CH_3)C(O)OCH_3 \rightarrow \text{Products} \quad (7)$$

$$OH + (E) - CH_3CH = CHCH_2OH \rightarrow \text{Products} \quad (8)$$

where $k_7 = (4.2 \pm 0.32) \times 10^{-11}$ (Teruel et al., 2006) and $k_8 = (9.8 \pm 1.5) \times 10^{-11}$ (Cometto et al., 2008). All the *k* values are in units of cm^3 $molecule^{-1}$ s^{-1}.

Table 1 shows the data on relative rate coefficients $k_{Alcohol}/k_{Reference}$ and absolute rate coefficients k_{VOC} at room temperature (298 K). The ratios were obtained from the average of several experiments using different initial concentrations of the alcohols. The rate constants obtained by averaging the values from different experiments were the following:

$$k_1 = \left(1.0 \pm 0.3\right) \times 10^{-10} cm^3\ molecule^{-1} s^{-1}$$

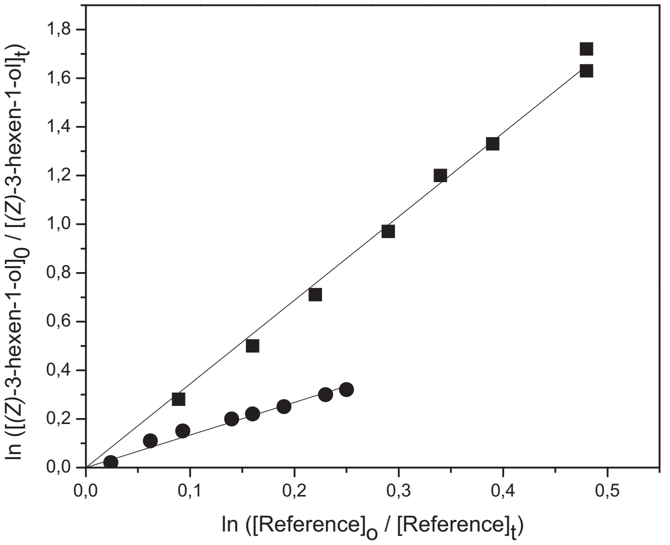


Fig. 3. Plot of the kinetic data for the reaction of (*Z*)-3-hexen-1-ol with OH radicals using methyl methacrylate (■) and (*E*)-2-buten-1-ol (●) as reference hydrocarbons.

Table 1
Rate constant ratio $k_{Alcohol}/k_{Reference}$ and rate constants for the reaction of OH radicals with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol at 298 ± 3 K in 760 ± 10 Torr of air.

Unsaturated alcohol	Reference	$k_{Alcohol}/k_{Reference}$	$k_{Alcohol}$ (cm^3 $molecule^{-1}$ s^{-1})
(*E*)-2-hexen-1-ol	$CH_2{=}C(CH_3)C(O)OCH_3$	(2.34 ± 0.09)	$(9.8 \pm 1.1) \times 10^{-11}$
	$CH_2{=}C(CH_3)C(O)OCH_3$	(2.26 ± 0.14)	$(9.5 \pm 1.3) \times 10^{-11}$
	$CH_3CH{=}CHCH_2OH$	(1.12 ± 0.15)	$(1.1 \pm 0.3) \times 10^{-10}$
	$CH_3CH{=}CHCH_2OH$	(1.08 ± 0.13)	$(1.1 \pm 0.3) \times 10^{-10}$
	Average		$(1.0 \pm 0.3) \times 10^{-10}$
(*E*)-3-hexen-1-ol	$CH_2{=}C(CH_3)C(O)OCH_3$	(2.67 ± 0.11)	$(1.1 \pm 0.1) \times 10^{-10}$
	$CH_2{=}C(CH_3)C(O)OCH_3$	(2.64 ± 0.07)	$(1.1 \pm 0.1) \times 10^{-10}$
	$CH_3CH{=}CHCH_2OH$	(1.19 ± 0.04)	$(1.2 \pm 0.2) \times 10^{-10}$
	$CH_3CH{=}CHCH_2OH$	(1.19 ± 0.05)	$(1.2 \pm 0.2) \times 10^{-10}$
	Average		$(1.2 \pm 0.2) \times 10^{-10}$
(*Z*)-3-hexen-1-ol	$CH_2{=}C(CH_3)C(O)OCH_3$	(3.62 ± 0.09)	$(1.5 \pm 0.2) \times 10^{-10}$
	$CH_2{=}C(CH_3)C(O)OCH_3$	(3.43 ± 0.10)	$(1.4 \pm 0.1) \times 10^{-10}$
	$CH_3CH{=}CHCH_2OH$	(1.33 ± 0.11)	$(1.3 \pm 0.3) \times 10^{-10}$
	$CH_3CH{=}CHCH_2OH$	(1.24 ± 0.07)	$(1.2 \pm 0.3) \times 10^{-10}$
	Average		$(1.4 \pm 0.3) \times 10^{-10}$

$$k_2 = \left(1.2 \pm 0.2\right) \times 10^{-10}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

$$k_3 = \left(1.4 \pm 0.3\right) \times 10^{-10}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have also considered the corresponding error on the reference rate constants (7–8). We prefer to quote rate constants for the reactions of OH with the hexenols ($k_{Alcohol(average)}$ in Table 1) which are averages of the determinations obtained using both reference compounds and have errors which encompass the extremes of the errors associated with each value of $k_{Alcohol}$. The errors for the ratios $k_{Alcohol}/k_{reference}$ are only 2σ statistical errors.

4.1. Comparison with previous determinations

Table 2 shows the comparison between the rate coefficients of the reactions of (*E*)-2-hexen-1-ol and (*Z*)-3-hexen-1-ol obtained in this work and those reported previously in literature.

For the reaction (1) of OH with (*E*)-2-hexen-1-ol, the value obtained in this work of $(1.0 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is in a relatively good agreement, within the experimental error, with the absolute value of $(6.15 \pm 0.75) \times 10^{-11}$ determined by PLP-LIF (Davis and Burkholder, 2011).

For the reaction (3) of OH radicals with (*Z*)-3-hexen-1-ol, there are a relative kinetic study (Atkinson et al., 1995) and an absolute determination using pulse laser photolysis coupled with laser induced fluorescence (PLP-LIF) as a detection technique (Jimenez et al., 2009). Recently, an absolute study using PLP-LIF technique, have been reported (Davis and Burkholder, 2011). It can be seen from Table 2, that our result of $(1.4 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^1 is in very good agreement, within the experimental error, with all results of $(1.08 \pm 0.22) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^1, $(9.57 \pm 2.42) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^1 and $(1.06 \pm 0.12) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^1.

To the best of our knowledge, there are no other prior reported values of the rate constants for the reaction (2) of OH radicals with (*E*)-3-hexen-1-ol. The present study, thus, is the first kinetic study of this reaction; therefore, no direct comparison with the literature can be made. Nevertheless, it is interesting to compare the reactivity of the hexenols studied in this work with similar unsaturated alcohols obtained from literature as well as with structure activity relationship (SAR) calculations to test agreement with these correlations.

4.2. SAR calculations and reactivity trends

The structure activity relationship (SAR) of Kwok and Atkinson (1995) was used to perform rate coefficients calculations. The *k* values were calculated using the Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91 (US Environmental Protection Agency, 2000) to be 6.99, 6.28 and 6.23, in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, for the reactions of OH with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol, respectively. These calculated values are close but still lower than the experimental values obtained in this work of (1.0 ± 0.3), (1.2 ± 0.2) and $(1.4 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

Table 3 lists the rate coefficients at 298 K obtained in this work for reactions (1–3) and for the reactions of OH with other C_3–C_7 unsaturated alcohols. From this table is possible to observe a very small difference between the rate coefficients of the hexenols measured. Eventough, comparing 2-hexen-1-ol and 3-hexen-1-ol the *k* increases from 1,0 to 1,2 consistent with the location of the OH electron with drawing group with respect to the double bond. The negative inductive effect of the OH group to the nucleophiclic center (π electrons of the double bond) is less pronounced when OH is far to the double bond ($k_{3\text{-hexen-1-ol}} > k_{2\text{-hexen-1-ol}}$).

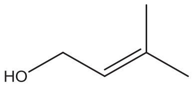
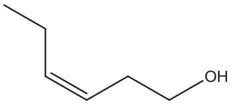
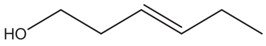
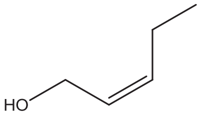
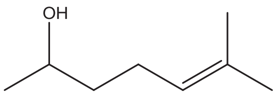
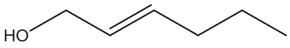
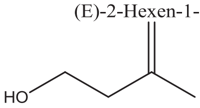
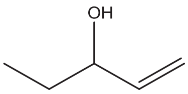
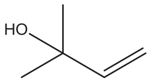
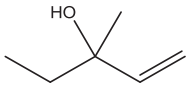
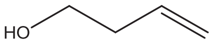
Comparing different (*E*/*Z*)-isomers, the decrease of the rate coefficients between the isomers (*Z*) to (*E*), with values from (1.4–1.2) $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, could be due to a difference in the steric hindrance toward the elecrophiclic attack by the OH radicals. Now considering, the rate coefficients of two pentenols (2-penten-1-ol and 3-penten-1ol), the 2 times higher rate coefficient of the non-terminal 2-penten-1-ol (1.06×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) compared with the 1-penten-3-ol (0.67×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) is possible to be explained by the substitution of the olefinic H atoms by alkyl radicals that donates electron density increasing the probability of the OH electrophilic attack. Furthermore, the low stability of the primary radical formed (for 1-penten-3-ol), affects reactivity lowering the reactivity compared with a higher stability of a secondary radical formed in a non-terminal unsaturated alcohol (2-penten-1-ol).

If we compare the reactivity of two structural isomers, like 2-penten-1-ol and 3-methyl-3-buten-1-ol, similar rate coefficients (1.06×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and 0.97×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) were obtained consistent with the same position of the OH and the distance with the double bond and the H atom substitution in the double bond by an electron donating alkyl group that increases the reactivity to the OH radical electrophilic attack. On the other hand, the structural similarities of 1-penten-3-ol, 2-

Table 2
Comparison of the kinetic results obtained in this work with previous determinations at room temperature.

	k (cm^3 molecule^{-1} s^{-1})	Technique	Reference
(E)-2-hexen-1-ol	$(1.0 \pm 0.3) \times 10^{-10}$	GG-FID	*This work*
	$(6.15 \pm 0.75) \times 10^{-11}$	PLP-LIF	Davis and Burkholder, 2011
(Z)-3-hexen-1-ol	$(1.4 \pm 0.3) \times 10^{-10}$	GC-FID	*This work*
	$(1.08 \pm 0.22) \times 10^{-10}$	RR-GC-FID	Atkinson et al., 1995
	$(9.57 \pm 2.42) \times 10^{-11}$	PLP-LIF	Jimenez et al., 2009
	$(1.06 \pm 0.12) \times 10^{-10}$	PLP-LIF	Davis and Burkholder, 2011

Table 3
Rate coefficients of the reactions of OH radicals with unsaturated alcohols at 298 K.

Unsaturated alcohol	$k_{OH} \times 10^{10}$ cm^3 molecule^{-1}	Reference
 3-methyl-2-buten-1-ol	1.5 ± 0.1	Imamura et al., 2004
 (Z)-3-Hexen-1-ol	1.4 ± 0.3	*This work*
 (E)-3-Hexen-1-ol	1.2 ± 0.2	*This work*
 (Z)-2-Penten-1-ol	1.06 ± 0.15	Orlando et al., 2001
 6-Methyl-5-hepten-2-ol	1.0 ± 0.3	Bernard et al., 2012
 (E)-2-Hexen-1-ol	1.0 ± 0.3	*This work*
 3-methyl-3-buten-1-ol	0.97 ± 0.07	Imamura et al., 2004
 1-penten-3-ol	0.67 ± 0.09	Orlando et al., 2001
 2-methyl-3-buten-2-ol	0.66 ± 0.05	Imamura et al., 2004
 3-Methyl-1-penten-3-ol	0.62 ± 0.18	Bernard et al., 2012
 3-buten-1-ol	0.59 ± 0.09	Cometto et al., 2008
 2-propen-1-ol	0.45 ± 0.06	Orlando et al., 2001

methyl-3-buten-1-ol, 3-methyl-1-penten-3-ol and 3-buten-1-ol is reflecting by obtaining almost no difference between the rate coefficients (0.67, 0.66, 0.62 and 0.59) × 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.

In general terms, the dependence of the rate constant with the C number of the unsaturated alcohol seems to be very weak, for instance observing the similar reactivities of hexenols and heptenols (Table 3).

More rate coefficients of other unsaturated alcohols are necessary to determine experimentally in order to better define the parameters that govern the reactivity of these biogenic VOCs with different oxidants and in particular with the atmospheric relevant species.

4.3. Correlation between k and E_{HOMO} calculations

The reactivity of different kinds of electrophiles such as O and Cl atoms, OH and NO_3 radicals and O_3 molecules toward alkenes, methyl-substituted alkenes and more recently to unsaturated oxygenated VOCs has been found to correlate with the ionization potentials (IP) or the energy of the highest occupied molecular orbital (HOMO) of the unsaturated VOC (Atkinson, 1997; Wayne et al., 1991; Baumgartner et al., 2002; Blanco et al., 2009). The E_{HOMO} for the reactions of the saturated and unsaturated VOCs are presented in the literature in the form:

$$\ln\ k\left(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\right) = aE_{\text{HOMO}} + b \tag{II}$$

Thus, the use of the rate coefficients determined in this work together with other values for different kinds of unsaturated alcohols from the literature enables a relationship with E_{HOMO} to be proposed for OH/unsaturated alcohols (Table 4). These correlations are presented in Fig. 4.

The HOMO energies for the alcohols listed in Table 4 were calculated using the Gaussian 03 package (Frisch et al., 2003). The geometry optimizations and initial values of energies were obtained at the Hartree–Fock (HF) level, and ab initio Hamiltonian with a 6-31++ G(d,p) bases set was used. The self-consistent field energies were then calculated by Moller–Plesset perturbation theory (MP4-SCF) using an “ab initio” Hamiltonian with a 6-311++ G(d,p) bases set. The correlations obtained in this work for this group of reactions are as follows:

$$\begin{aligned}\ln\ k_{\text{OH}}\left(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\right) = &-\left(1.3 \pm 0.1\right)E_{\text{HOMO}} \\ &-\left(10.3 \pm 1.3\right)\end{aligned} \tag{III}$$

This is in a reasonable agreement with the correlation obtained previously (Blanco et al., 2009) for the OH reactions with unsaturated esters, alkenes and other VOCs of:

Table 4
Plot of $-\ln(k_{OH+Alcohol}$ cm^{-3} molecule^{-1} s^{-1}) *versus* the calculated values of $-E_{HOMO}$ of the reactions of OH radicals with unsaturated alcohols.

Unsaturated alcohol	k_{OH} (cm^3 molecule^{-1} s^{-1})	$-E_{HOMO}$ (eV)
3-Hexen-1-ol	1.4×10^{-10}[a]	9.44
2-Hexen-1-ol	1.0×10^{-10}[a]	9.58
3-Methyl-1-penten-3-ol	6.2×10^{-11}[b]	10.01
1-Penten-3-ol	5.7×10^{-11}[c]	10.18
1-Propen-3-ol	3.7×10^{-11}[d]	10.35

[a] This work.
[b] Bernard et al. (2012).
[c] Jimenez et al. (2009).
[d] Upadhyaya et al. (2001).

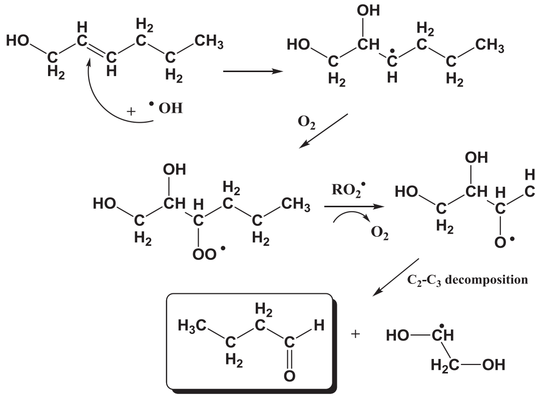
$$\ln k_{OH}\left(\mathrm{cm^3 molecule^{-1} s^{-1}}\right) = -\left(1.1 \pm 0.2\right)E_{HOMO} - \left(12.6 \pm 1.7\right) \tag{IV}$$

This correlation can be used to calculate rate coefficients of OH + unsaturated alcohols reactions that have not been measured yet from its experimental difficulties. Hence, it can help to modelers to obtain rate coefficients with a reasonable accuracy.

4.4. Products determination

In addition, experiments were also conducted to identify reaction products under similar conditions to the kinetic experiments for the reactions (1)–(3). Butanal was found as the main product of the reaction of OH radicals with (*E*)-2-hexen-1-ol. In similar conditions, propanal was identified as unique product of the gas-phase reactions of OH with (*E*)-3-hexen-1-ol and (*Z*)-3-hexen-1-ol. We observed the ions with $m/e = 72$, 57 and 44 for butanal; and $m/e = 58$, 57 and 29 for propanal.

The reaction products found, together with the observed reactivity trends, confirm that the reaction proceeds via an addition mechanism of the OH radical to the double bond similar to that proposed by Atkinson for the OH radical addition to unsaturated alcohols (Atkinson et al., 1995). The 2,3-hydroxyalcoxy radical formed in the OH addition step, decomposes in the presence of O_2 in NO_x-free air, leading mainly to the corresponding aldehydes. The following reaction scheme of the OH- initiated degradation of (*E*)-2-hexen-1-ol is shown as an example:



According to the products observed, the main fate of the 2,3-hydroxyalcoxy radicals formed seems to be the C_2—C_3 decomposition channel. We did not observe other products corresponding to C_3—C_4 decomposition ($HC(O)CH_2CH_2OH$), isomerization or reaction with oxygen (dihydroxycarbonyl compounds) channels. Moreover, previous studies of (*Z*)-3-hexen-1-ol oxidation initiated by OH radical performed by FTIR and API-MS and direct air sampling by Aschman (Aschmann et al., 1997) have shown the formation of 3-hydroxyethanal as a co-product of the degradation of β-hydroxyalkyl radicals as well as a small amount isomerization and O_2 reaction products. These results are in agreement with our present result.

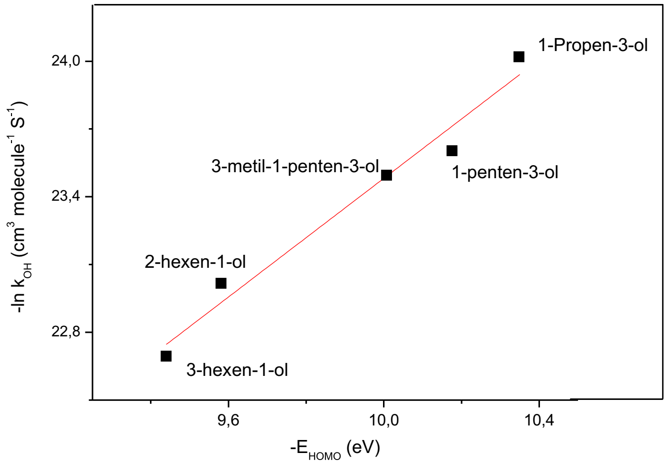


Fig. 4. Correlation plot of ln (k cm^{-3} molecule^{-1} s^{-1}) *versus* calculated E_{HOMO} for the reactions of OH radicals (■) with unsaturated VOCs.

Further experiments using different experimental techniques and tropospheric conditions, including in the presence of NO_x, would be desirable to obtain the product distribution, mechanisms and a better understanding of the atmospheric implications associated with these biogenic organics on air quality at different urban and remote areas.

4.5. Atmospheric implications

In the atmosphere, unsaturated alcohols are expected as alkenes, to be removed in the gas-phase by chemical reactions with OH radicals, NO_3 radicals and O_3 molecules or by solar photolysis. Other sinks can be wet and dry deposition.

Considering the gas-phase loss processes, the lifetimes toward reaction with OH, NO_3 and O_3 have been calculated for the hexenol series. Tropospheric lifetimes were calculated using the expression: $\tau_x = 1/k_x[X]$ with $X =$ OH, NO_3 and O_3, 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.

In these calculations, the following rate constant values were used: $k_{OH} = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this work) and $k_{NO3} = 1.30 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Pfrang et al., 2006) for (*E*)-2-hexen-1-ol; $k_{OH} = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this work) and $k_{NO3} = 1.56 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Pfrang et al., 2006) for (*E*)-3-hexen-1-ol; $k_{OH} = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this work) and $k_{NO3} = 2.67 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Pfrang et al., 2006) and $k_{O3} = 6.39 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1995) for (*E*)-3-hexen-1-ol. Typical atmospheric concentrations were used, a 12 h average concentration of OH $[OH] = 2 \times 10^6$ molecule cm^{-3} (Hein et al., 1997), $[NO_3] = 5 \times 10^8$ molecule cm^{-3} (Shu and Atkinson, 1995) and a 24 h average O_3 concentration of 7×10^{11} molecule cm^{-3} (Logan, 1985).

Table 5
Estimated tropospheric lifetimes of the unsaturated alcohols studied in this work with OH radicals, NO_3 radicals and O_3.

Alcohol	τ_{OH} (h)	τ_{NO3} (h)	τ_{O3} (h)
(*E*)-2-hexen-1-ol	1.4	4.3	–
(*E*)-3-hexen-1-ol	1.2	1.3	–
(*Z*)-3-hexen-1-ol	1.0	2.1	6.2

The estimated tropospheric lifetimes at room temperature of the unsaturated alcohols with the tropospheric oxidants OH, NO_3 and O_3, are listed in Table 5. Loss of these compounds by photolysis can be considered negligible since they are photolytically stable in the actinic region of the electromagnetic spectrum. Concerning the atmospheric fate of (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, the lifetimes, in the range of few hours, indicates that hexenols are likely to be removed rapidly in the gas-phase, with the three oxidant species competing as loss processes for the three unsaturated alcohols studied in this work. The OH-initiated oxidation during day time hours and in night-time troposphere NO_3-initiated degradation of hexenols can be a significant if not the dominant homogeneous loss process. Nevertheless, in polluted areas, where peak concentrations of O_3 molecules as high as 5×10^{12} molecules cm^{-3} can occur, O_3 molecules-initiated degradation of hexenols can compete as an atmospheric sink of these unsaturated alcohols.

The short estimated lifetimes have shown that these compounds will be degraded close to their emission sources with a local scale impact. Consequently, the fate of the products arising from the OH-initiated oxidation of the VOCs studied will be important since the atmospheric oxidation of these products can also contribute to ozone, long-lived nitrogen containing compounds and other oxidants in the troposphere. The photodegradation of the carbonyls photodegradation products of hexenols, in the presence of high NO_x concentrations, could produce peroxyacetyl nitrate (PAN) and derivatives that can affect the air quality by photochemical smog production together with tropospheric ozone (Grosjean et al., 1993). Furthermore, these carbonyls can affect the oxidation capacity of the troposphere by affecting the HOx cycles.

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