



FTIR gas kinetic study of the reactions of ozone with a series of hexenols at atmospheric pressure and 298 K



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ABSTRACT

Relative rate coefficients of the reactions of O₃ with (*Z*)-3-hexen-1-ol, (*E*)-3-hexen-1-ol and (*E*)-2-hexen-1-ol have been determined in an environmental chamber with in situ FTIR detection of the reactants at 298 K and 760 Torr. The following rate coefficients (in units of 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) have been determined: (6.04 ± 0.95) for (*Z*)-CH₂(OH)CH₂CH=CHCH₂CH₃; (5.83 ± 0.86) for (*E*)-CH₂(OH)CH₂CH=CHCH₂CH₃; (5.98 ± 0.73) for (*E*)-CH₂(OH)CH=CH(CH₂)₂CH₃. This is the first kinetic study for the reactions of O₃ with (*E*)-2-hexen-1-ol and (*E*)-3-hexen-1-ol. Reactivity trends are developed and the atmospheric persistence of these compounds is calculated based on the rate coefficients.

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1. Introduction

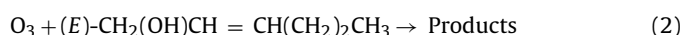
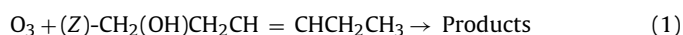
The study of oxygenated volatile organic compounds (OVOCs) in the atmosphere of biogenic origin, and the degradation products resulting from their tropospheric oxidant mediated photooxidation, is of importance due to the high reactivity and ozone formation potential of many of these compounds which makes them substantial contributors to the formation of photochemical smog and secondary organic aerosol (SOA) [1].

Among the oxygenated organic compounds emitted by plants, and known as green leaf volatiles (GLVs) are three isomers of hexenol: (*E*)-2-hexen-1-ol, (*Z*)-3-hexen-1-ol and (*E*)-3-hexen-1-ol. Previous studies demonstrated that the amounts of these compounds increase when plants suffer any mechanical damage or a plague attack, depending also on the prevailing conditions of temperature and sunlight [2]. Accordingly, substantial amounts of unsaturated OVOCs from biogenic sources are continually being introduced into the atmosphere. Previous works have estimated a global emission rate of 520 Tg C/year [3].

There have been a number of studies and evaluation of data on the reactions of ozone with unsaturated alcohols reported in the literature [4–11]. However, reactivity and mechanistic information for the reaction of ozone with the hexenols isomers is limited.

Grosjean et al. [4] have reported a determination of the rate coefficient for the reaction of ozone with (*Z*)-3-hexen-1-ol using an absolute method and Atkinson et al. [11] have reported a determination of the rate coefficient for the same reactions using a relative kinetic technique. Both studies, were performed at atmospheric pressure and 298 K, however, there is a significant discrepancy in the reported values, that of Grosjean et al. [4] is around 40% higher than that of Atkinson et al. [11]. Grosjean et al. [5] have investigated the products formed in the reaction of ozone with (*Z*)-3-hexen-1-ol and also those formed in the sunlight irradiation of a (*Z*)-3-hexen-1-ol/NO/air mixture. To the best of our knowledge these are the only studies available in the literature on the atmospheric chemistry of the hexenols and their oxidation processes initiated by ozone molecules.

There is obviously a need for further studies on these important GLVs not only to better establish the rate coefficient for the reaction of ozone with (*Z*)-3-hexen-1-ol but also to extend kinetic and mechanistic ozonolysis studies to other hexenol isomers. Here we provide a new determination of the rate coefficient for the reaction of ozone with (*Z*)-3-hexen-1-ol and present the first kinetic study of the reaction of ozone with (*E*)-2-hexen-1-ol and (*E*)-3-hexen-1-ol; reactions (1), (2) and (3), respectively. All of the reactions have been studied at room temperature and atmospheric pressure of air:



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Additionally, our work aims to better define the reactivity of $\text{RCH}=\text{CHR}'$ compounds towards ozone molecules where R and $\text{R}'=\text{H}$, alkyl and/or oxygenated substituents. In this sense, the results are also discussed in terms of substituent effects on the reactivity of olefinic compounds towards ozone. Lifetimes of the VOCs studied in this work, with respect to reaction with the important atmospheric oxidants, have been calculated taking into account the experimental rate coefficients obtained and typical average oxidant tropospheric concentrations.

2. Experimental

All the experiments were performed in a 480L chamber at a total pressure of 760 Torr (760 Torr = 101.325 kPa) and 298 ± 3 K in synthetic air. A detailed description of the reactor can be found elsewhere and only a brief general overall description is given here [12]. The chamber is composed of a cylindrical borosilicate glass vessel (3 m in length and 45 cm inner diameter) closed at both ends by aluminium flanges. The metal flanges contain ports for the introduction of bath gases and reactants into the chamber.

A pumping system consisting of a roots pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. A magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer (Thermo Scientific Nicolet 6700) equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector enables in situ monitoring of the reactants in the infrared range $4000\text{--}700\text{ cm}^{-1}$. The White mirror system was operated with the total optical absorption path length set to 48.11 m and infrared spectra were recorded with a spectral resolution of 1 cm^{-1} . Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15 such spectra were recorded per experiment. An electrical discharge in a flow of pure oxygen was used to generate ozone and introduced into the reactor through a quantity control valve.

The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were: (Z)-3-hexen-1-ol (3–4), (E)-2-hexen-1-ol (3–4), (E)-3-hexen-1-ol (3–4), 1,4-cyclohexadiene (4–5), isoprene (4–5); ozone was added stepwise in 6 additions of $30\text{--}50\text{ cm}^3$ volume in O_2 diluent per experiment resulting in 40–75% reduction in the initial concentration of the unsaturated alcohol.

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): (Z)-3-hexen-1-ol at 1053.6 and 3616.5, (E)-2-hexen-1-ol at 1388.7 and 3653.7, (E)-3-hexen-1-ol at 1385.8 and 3619.3, 1,4-cyclohexadiene at 965.5 and 3038 and isoprene at 897 and 3098.

The relative kinetic technique has been used to determine rate coefficients for the reactions of O_3 with (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol and (E)-3-hexen-1-ol using 1,4-cyclohexadiene and isoprene as reference compounds:



Provided that the alcohol and reference compound are lost only by reactions (4) and (5), respectively, then it can be shown that:

$$\ln \left\{ \frac{[\text{Alcohol}]_0}{[\text{Alcohol}]_t} \right\} = \frac{k_4}{k_5} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (1)$$

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_4 and k_5 are the rate coefficients of reactions (4) and (5), respectively.

The relative rate technique relies on the assumption that the alcohol and the reference compounds are removed solely by reaction with ozone. No loss of either the hexenols or the reference compounds was observed on leaving mixtures of the compounds in the dark for 1 h in the absence of ozone showing that wall loss of the compounds was negligible. The reaction of O_3 with olefinic compounds is known to produce OH radicals [13], thus reactions of both the hexenols and the reference compounds 1,4-cyclohexadiene and isoprene will produce OH radicals in the reaction systems which can react with the hexenols and reference compounds and interfere with the kinetic analysis. Normally in this type of experiment either CO or an organic compound such as cyclohexane is added in excess to scavenge any OH radicals formed. However, both the hexenol isomers and the reference compounds 1,4-cyclohexadiene and isoprene all react with OH radicals at rates that are close to the gas kinetic limit [14,15]. These high rate coefficients mean that approximately 4000 ppmV CO (~ 30 Torr) and 700 ppm cyclohexane would need to be added to the reactor to scavenge more than 90% of the OH radicals formed. Apart from the safety risk associated with the large quantities of CO in the reactor such concentrations would render monitoring of the hexenols and reference compounds in the infrared impossible.

Since we have not added sufficient scavenger, the terms for the decay of the hexenol and the reference compound should be corrected by inclusion of the terms: $-k_{\text{hexenol}} \int [\text{OH}] dt$ and $-k_{\text{reference}} \int [\text{OH}] dt$ in the left hand and right hand sides of Eq. (1), respectively, where k_{hexenol} and $k_{\text{reference}}$ are the rate coefficients for reaction of OH with the hexenol and reference compound, respectively, and $[\text{OH}]$ is the OH radical concentration. Both isoprene and 1,4-cyclohexadiene have OH rate coefficients at room temperature of $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [15] while those of OH with (E)-2-hexen-1-ol, (E)-3-hexen-1-ol and (Z)-3-hexen-1-ol (in $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are (1.0 ± 0.3) , (1.2 ± 0.2) and (1.4 ± 0.3) , respectively [14]. It was reported that the OH yield for the reaction of O_3 with (Z)-3-hexen-1-ol is $\sim 26\%$ [11], and it is to be expected that the yield for the hexenol isomers will be similar. We could not find an OH yield for the reaction of O_3 with 1,4-cyclohexadiene but we suspect it will be similar to that for mono-cycloalkenes which is around 40% [13]. The OH radical yields for the reaction of O_3 with the conjugated dienes are fairly low [13] and a value of 26% is the currently recommended value for isoprene [16].

Since the integral OH radical concentrations will be the same for both the hexenols and the reference compounds and the OH rate coefficients are very similar we argue that the correction factors for reaction with OH are essentially self-cancelling and will only marginally affect the measured rate coefficients for reaction of the hexenols with O_3 . The relatively low OH radical yields for most of the olefinic compounds used in the investigations will also help to lessen any interference.

3. 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%), isoprene (Alfa Aesar, 99%), 1,4-Cyclohexadiene (Alfa Aesar, 97%), (Z)-3-hexen-1-ol (Alfa Aesar, 98%), (E)-2-hexen-1-ol (Alfa Aesar, 97%) and (E)-3-hexen-1-ol (Alfa Aesar, 97%).

4. Results and discussion

Figures 1–3 show typical plots of the kinetic data obtained for the reaction of ozone with (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol and (E)-3-hexen-1-ol, respectively, plotted according to Eq. (1). For clarity, each plot shows one example for each of the two reference

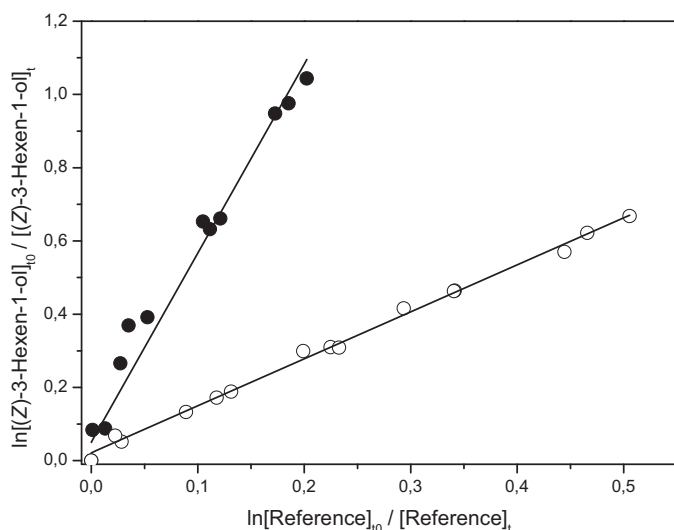


Figure 1. Plots of the kinetic data for the reaction of O_3 with (Z)-3-hexen-1-ol using 1,4-cyclohexadiene (\circ) and isoprene (\bullet) as reference compounds at 298 K and atmospheric pressure of air.

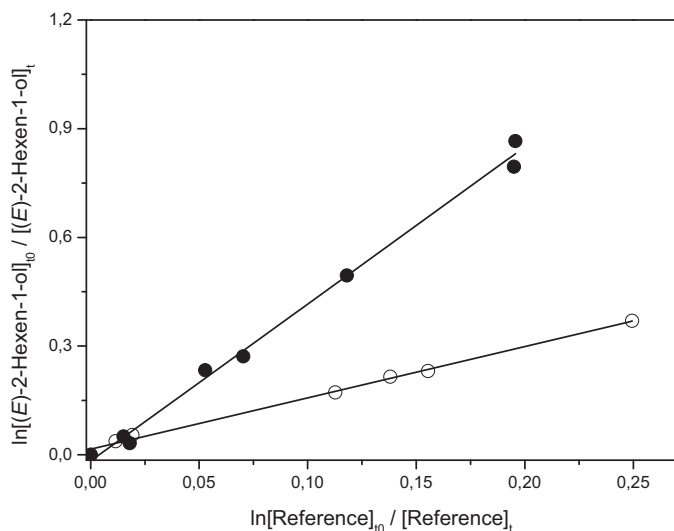


Figure 2. Plots of the kinetic data for the reaction of O_3 with (E)-2-hexen-1-ol using 1,4-cyclohexadiene (\circ) and isoprene (\bullet) as reference compounds at 298 K and atmospheric pressure of air.

compounds employed. Two experiments have been performed for each hexenol isomer and reference compound combination. Good linear relationships with near-zero intercepts were obtained in all cases.

Table 1 lists the relative rate coefficients k_4/k_5 obtained from plots of the kinetic data for each hexenol isomer and reference compound combination. The absolute rate coefficients $k_{Alcohol}$ for the reaction of O_3 with the hexenols have been obtained using values of $(4.75 \pm 0.23) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17] and $(1.27 \pm 0.08) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8] for the reactions of O_3 with 1,4-cyclohexadiene and isoprene, respectively. The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which a contribution has been added to cover uncertainties in the reference rate coefficients.

As can be seen from Table 1 there is relatively good agreement between the values of the rate coefficients obtained for the 2 determinations with each reference compound for the hexenols, the values obtained with 1,4-cyclohexadiene as the

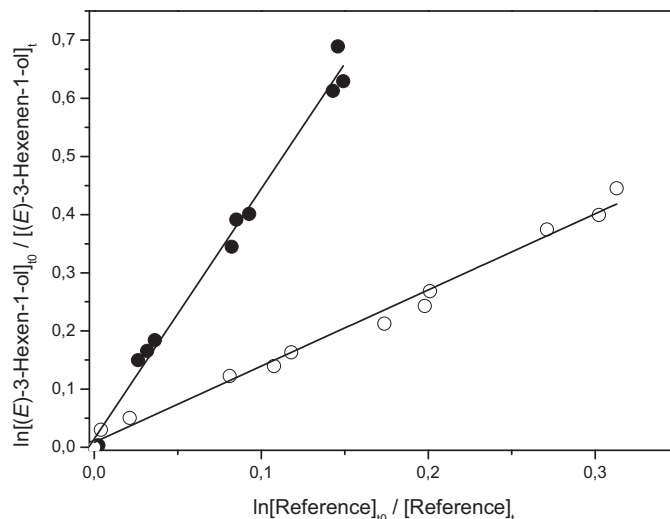


Figure 3. Plots of the kinetic data for the reaction of O_3 with (E)-3-hexen-1-ol using 1,4-cyclohexadiene (\circ) and isoprene (\bullet) as reference compounds at 298 K and atmospheric pressure of air.

reference compound being $\leq 15\%$ higher than those obtained with isoprene as the reference compound. In addition, this agreement between the values obtained with the reference compounds 1,4-cyclohexadiene and isoprene, even though the rate coefficients for the reactions of O_3 with these references differ by a factor of approximately 4, serves to demonstrate that the interference by OH radicals in the rate coefficient determinations, as argued in the experimental section, is marginal for the hexenol/reference compound combinations used in the kinetic investigations.

We prefer to quote final rate coefficients for the reactions of O_3 with the hexenol isomers which are averages of all four determinations for each isomer:

$$k_1 = (6.04 \pm 0.95) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (5.98 \pm 0.73) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (5.83 \pm 0.86) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To the best of our knowledge, no kinetic data on the reaction of O_3 molecules with (E)-2-hexen-1-ol and (E)-3-hexen-1-ol have been previously reported. Thus, the present study is the first measurement of the rate coefficients for reactions (2) and (3) and no direct comparison with literature values can be made. However, the value obtained in this study for (Z)-3-hexen-1-ol of $k_1 = (6.04 \pm 0.95) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in excellent agreement with that reported by Atkinson et al. [11] of $k_1 = (6.4 \pm 1.7) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained at $296 \pm 2 \text{ K}$ and atmospheric pressure of air relative to the reaction of O_3 with (Z)-2-butene using GC-FID analysis and cyclohexane to scavenge any OH radicals formed. Grosjean et al. [4] have reported a value of $k_1 = (1.05 \pm 0.07) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction of O_3 with (Z)-3-hexen-1-ol obtained under pseudo-first-order conditions in a Teflon chamber at atmospheric pressure and 298 K which is a 40% higher than the value obtained in this work and also by Atkinson et al. [11] using relative kinetic techniques. There is no obvious reason for this discrepancy, however, while Grosjean et al. [4] monitored the decay of O_3 both of the relative measurements monitored the decay of the hexenol and reference compounds using GC-FID [11] and in situ FTIR (this work).

Given that within experimental errors, the rate coefficients for the reactions of O_3 with (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol and (E)-3-hexen-1-ol are identical, the results support a hypothesis that the

Table 1Reference compound, measured rate coefficient ratios, k_4/k_5 , and rate coefficients for the reactions of O_3 with unsaturated alcohols at 298 K in 760 Torr of air.

VOCs	Reference	k_4/k_5	k_{Alcohol} $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
(Z)-3-hexen-1-ol	Isoprene	4.68 ± 0.20	5.95 ± 0.62
	Isoprene	4.70 ± 0.16	5.98 ± 0.58
	1,4-Cyclohexadiene	1.33 ± 0.04	6.32 ± 0.31
	1,4-Cyclohexadiene	1.28 ± 0.02	6.10 ± 0.30
	Average		6.04 ± 0.95
(E)-2-hexen-1-ol	Isoprene	4.41 ± 0.17	5.60 ± 0.57
	Isoprene	4.60 ± 0.87	5.84 ± 0.15
	1,4-Cyclohexadiene	1.37 ± 0.03	6.52 ± 0.32
	1,4-Cyclohexadiene	1.31 ± 0.03	6.21 ± 0.30
	Average		5.98 ± 0.73
(E)-3-hexen-1-ol	Isoprene	4.29 ± 0.12	5.45 ± 0.50
	Isoprene	4.41 ± 0.16	5.60 ± 0.56
	1,4-Cyclohexadiene	1.28 ± 0.10	6.06 ± 0.29
	1,4-Cyclohexadiene	1.31 ± 0.04	6.22 ± 0.30
	Average		5.83 ± 0.86

Table 2Comparison of the rate coefficients for the reactions of O_3 with C_6 unsaturated alkenes, unsaturated aldehydes and alcohols.

Alcohol	$k_{\text{Ozone}} \times 10^{17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Aldehyde	$k_{\text{Ozone}} \times 10^{18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Alkene	$k_{\text{Ozone}} \times 10^{16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
(Z)-3-hexen-1-ol	$(6.04 \pm 0.95)^a$	(Z)-3-hexenal	$(35 \pm 2)^b$	(Z)-3-hexene	$(1.44 \pm 0.17)^d$
(E)-2-hexen-1-ol	$(5.98 \pm 0.73)^a$	(E)-2-hexenal	$(2.0 \pm 1.0)^c$	(E)-2-hexene	$(1.51 \pm 0.05)^e$
(E)-3-hexen-1-ol	$(5.83 \pm 0.86)^a$			(E)-3-hexene	$(1.57 \pm 0.25)^d$

^a This work.^b Xing et al. [19].^c Atkinson et al. [11].^d Grosjean et al. [20].^e Mc Gillen et al. [21].

double bond and the spatial arrangement of the atoms in these compounds have no influence on their reactivity towards O_3 . However, it is interesting to compare the reactivity of analogous C_6 unsaturated compounds towards ozone with that of the C_6 unsaturated alcohols studied on this work, since they will react via similar addition mechanisms [18]. Table 2 shows a comparison between values of the rate coefficients for C_6 alkenes and aldehydes available in literature and those for the unsaturated alcohols studied in this work. It can be seen from Table 2 that the room temperature rate coefficients for the hexenes are factors of between 2.4 and 2.7 faster than those of the rate coefficients for the corresponding unsaturated hexenols. The lower reactivity of the hexenols towards O_3 can be attributed to the negative inductive effect of $-OH$ group on the $>C=C<$ group which decreases the availability of π electrons for the electrophilic addition of O_3 to the unsaturated alcohols. The rate coefficient for the reaction of O_3 with (Z)-3-hexenal is almost a factor of two lower with respect to that for its analogue reaction with (Z)-3-hexen-1-ol, which is not surprising since it is well established that the contribution to the negative inductive effect of carbonyl-containing groups ($-CHO$ or $-C(O)OR$) is greater than that of a $-OH$ group [22]. The difference is even more obvious for (E)-2-hexenal where the $-CH(O)$ group is directly attached to the double bond and the rate coefficient for reaction with O_3 is a factor of 30 slower than that for the corresponding unsaturated alcohol (E)-2-hexen-1-ol. A similar comparison for (E)-3-hexen-1-ol with its analogue aldehyde has not been possible since there no rate coefficient for the reaction of O_3 with (E)-3-hexenal available in the literature.

Atmospheric lifetimes for the three hexenol isomers studied on this work with respect to gas phase removal through reaction with the major tropospheric oxidants OH radicals, NO_3 radicals, O_3 molecules and Cl atoms have been calculated using the expression $\tau_x = 1/k_x[X]$ where $X = OH, NO_3, O_3$ and Cl and 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 calculating the lifetimes for the reaction of O_3 with the three hexenols the rate coefficients reported in this study were used. In calculating the lifetimes for reaction of the hexenols with OH, NO_3 and Cl the following rate coefficients were used in the calculations: $k_{OH} = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14], $k_{NO_3} = 1.30 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [23], and $k_{Cl} = 3.49 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24] for (E)-2-hexen-1-ol; $k_{OH} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14], $k_{NO_3} = 1.56 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [23], and $k_{Cl} = 3.42 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24] for (E)-3-hexen-1-ol; and $k_{OH} = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14], $k_{NO_3} = 2.67 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [23], and $k_{Cl} = 2.94 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24] for (Z)-3-hexen-1-ol. The following typical atmospheric concentrations of the oxidants were used, a 12 h average OH concentration of $2 \times 10^6 \text{ molecule cm}^{-3}$ [25], $[NO_3] = 5 \times 10^8 \text{ molecule cm}^{-3}$ [26] and a 24 h average O_3 concentration of $7 \times 10^{11} \text{ molecule cm}^{-3}$ [27] and an average of chlorine atoms concentration of $[Cl] = 1 \times 10^4 \text{ molecule cm}^{-3}$ [28].

The estimated individual tropospheric lifetimes at room temperature of the unsaturated alcohols with respect to degradation by the tropospheric oxidants OH, NO_3 , O_3 and Cl, are listed in Table 3. The hexenols are photolytically stable in the actinic region of the electromagnetic spectrum, hence, loss by photolysis can be considered as negligible. The lifetimes of a couple of hours for the

Table 3Estimated tropospheric lifetimes of the unsaturated compounds studied in this work with O_3 molecules, Cl atoms, OH radicals and NO_3 radicals.

Alcohol	τ_{OH} (h)	τ_{NO_3} (h)	τ_{O_3} (h)	τ_{Cl} (h)
(Z)-3-hexen-1-ol	1.0	2.1	6.6	95
(E)-2-hexen-1-ol	1.4	4.3	6.7	81
(E)-3-hexen-1-ol	1.2	1.3	6.9	81

gas-phase reactions with OH and NO₃ radicals indicates that the hexenols will mainly be rapidly removed by reaction with OH radicals during the day and NO₃ radicals during the night. Reaction with O₃ will also make a fairly significant contribution during both day and night and during pollution episodes with high O₃ levels loss through reaction with O₃ may even become compatible with that through reaction with OH and NO₃. In most circumstances Cl-atom initiated degradation will be a negligible lost process. Even in areas where the high chlorine levels can be expected, such as in marine and some industrialised regions, it is unlikely that Cl-mediated loss can compete effectively with the OH-mediated loss due to the very high reactivity of OH towards the hexenols.

The very short lifetimes of the hexenol, in order of a few hours, means that they will be degraded near to their source of emission and will affect tropospheric chemical processes on local scale. Major oxidation products, however, are likely to be aldehydes which will be active in radical recycling and in polluted regions can form thermally stable peroxyacyl nitrates in substantial yield, which can contribute to the long range transport of NO_x.

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