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Kinetics and product identification of the reactions of (*E*)-2-hexenyl acetate and 4-methyl-3-penten-2-one with OH radicals and Cl atoms at 298 K and atmospheric pressure

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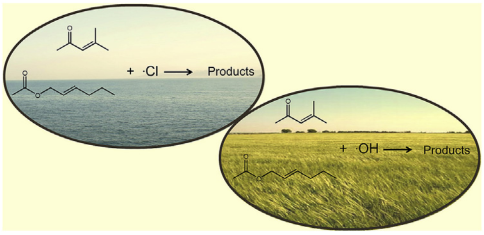
HIGHLIGHTS

- First kinetic study of the OH and Cl reactions with the title biogenic carbonyls.
- Reactivity of unsaturated BVOC increases with substitution by alkyl groups.
- Product study shows dominance of decomposition channels of alkoxy radicals formed.
- Atmospheric lifetimes of 1–2 h indicate degradation close to the emission sources.
- Carbonyls formed will contribute to tropospheric oxidation capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Rate coefficients for the reactions of hydroxyl radicals and chlorine atoms with two biogenic volatile organic compounds as (*E*)-2-hexenyl acetate and 4-methyl-3-penten-2-one have been determined at 298 K and atmospheric pressure. The decay of the organics was followed using a chromatograph with a flame ionization detector (GC-FID) and the rate constants were determined using a relative rate method. Rate coefficients are found to be (in cm^3 $molecule^{-1}$ s^{-1}): k_1(OH + (*E*)-2-hexenyl acetate) = $(6.88 \pm 1.41) \times 10^{-11}$, k_2(Cl + (*E*)-2-hexenyl acetate) = $(3.10 \pm 1.13) \times 10^{-10}$, k_3(OH + 4-methyl-3-penten-2-one) = $(1.02 \pm 0.20) \times 10^{-10}$ and k_4(Cl + 4-methyl-3-penten-2-one) = $(2.66 \pm 0.90) \times 10^{-10}$ at 298 K. This is the first kinetic experimental study for these reactions studied under atmospheric pressure. The rate coefficients are compared with previous determinations for other unsaturated and oxygenated compounds and reactivity trends are presented. Products identification studies were performed using solid-phase microextraction (SPME) method employing on-fiber products derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride using gas chromatograph with a mass spectrometer detector (GC-MS) for the reactions studied. In addition, atmospheric lifetimes of the unsaturated compounds studied are estimated and compared with other tropospheric sinks for these compounds.

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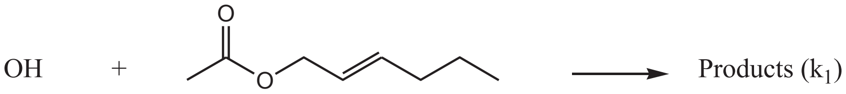
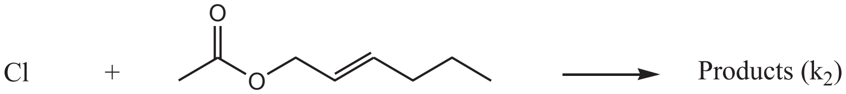
1. Introduction

Biogenic Volatile Organic Compounds (BVOCs), as isoprene, terpenes, and oxygenated compounds, are release to the atmosphere in large quantities with an importance to the chemical and physical properties of the atmosphere. In the presence of NO_x, from fossil fuel combustion and/or natural processes (Niinemets and Monson, 2013), BVOCs react in the atmosphere with different oxidants to lead tropospheric ozone and other photooxidants. These reactions may also produce a decrease in the concentrations of the hydroxyl radical (OH) and consequently the accumulation of methane and other greenhouse gases. A further effect of these reactions is the formation of secondary organic aerosol particles, a component of PM10 in the atmosphere, which has known adverse effects on human health. BVOC emissions take place on the continental scale and can therefore play a role in atmospheric chemistry even in remote areas (Niinemets and Monson, 2013).

Particularly, *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one are an unsaturated ester and an unsaturated ketone, respectively that have been identified in biogenic emissions to the atmosphere (Ciccioli et al., 1993, 1994; Koenig et al., 1995; Croft et al., 1993). *(E)*-2-hexenyl acetate is emitted by silver birch (B. pendula) (Maja et al., 2015) and 4-methyl-3-penten-2-one is also a specific Microbial Volatile Organic Compounds (MVOCs) produced by *C. pratensis* involved in the plant growth and productivity (Kanchiswamy et al., 2015).



(1)



(2)

(3)

(4)

Once emitted into the atmosphere, these BVOCs could react with OH and NO_3 radicals, O_3 molecules or Cl atoms. The reactions of the OH radical are of central importance with respect to the oxidation of volatile organic compounds (VOC) in the troposphere. The degradation of most VOCs is initiated by the highly reactive OH radical. (Finlayson-Pitts and Pitts, 2000). However, reaction of VOCs initiated by Cl atoms also plays an important role. It is well known that chlorine concentrations increase in certain regions, as the marine boundary layer and coastal regions (Vogt et al., 1996; Spicer et al., 1998), and close to industrial areas where chlorine can be emitted directly from incineration and power generation (Sarwar and Bhave, 2007; Riedel et al., 2013). Besides, recent studies of the nitryl chloride ($ClNO_2$) in marine and mid-continental air (Thorston et al., 2010; Philips et al., 2012) and in urban plants plumes (Riedel et al., 2013) have highlighted the potential importance of $ClNO_2$ as a hither to unconsidered source of Cl atoms. A study of Cl_2 and $ClNO_2$ in the coastal marine boundary layer from field measurements and modelling studies has been reported for Los Angeles region (Riedel et al., 2012). The results indicated that over the course of an entire model day $ClNO_2$ accounted for 45% of the integrated Cl-atom production showing that Cl-atom mediated chemistry could contribute quite substantially to the photooxidation of VOCs in this region particularly in the early morning.

The present study aim to investigate the kinetic behavior of these BVOCs towards the OH radical and Cl atoms under simulated tropospheric conditions.

In this sense, we report here the room temperature and atmospheric pressure determinations of the rate coefficients for the reactions of OH radicals and Cl atoms with *(E)*-2-hexenyl acetate ($CH_3C(O)OCH_2CH{=}CHCH_2CH_2CH_3$) and 4-methyl-3-penten-2-one ($CH_3C(CH_3){=}CHC(O)CH_3$):

To the best of our knowledge the rate coefficients for the reactions of OH radicals and Cl atoms with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one have not been reported previously in the literature. Therefore, this is the first determination of the rate coefficients for the reactions (1)–(4).

Kinetic investigations of the OH radical and Cl atom reaction with BVOCs are essential for the evaluation of the significance of BVOCs on air pollution. The rate coefficient of the OH radical and Cl atom reaction with BVOCs influences their distribution in the troposphere, their transport distance and may indicate the potential of BVOCs to contribute to smog formation. Additionally, the product identification study will increase the mechanistic and product data base for the reactions of OH radicals and Cl with unsaturated oxygenated VOCs under NO_x-free conditions. The presence of $(CH_3)_2C{=}CH$- unit in 4-methyl-3-penten-2-one give a high potential to form acetone which plays an important role in determining the oxidative capacity of the atmosphere (Arnold et al., 1997; Folkins and Chatfield, 2000).

Tropospheric implications of the reactions studied were assessed taking into account the residence lifetimes determined by the reactions of the unsaturated VOCs studied with the main tropospheric oxidants.

2. Experimental section

The kinetic experiments were performed by the relative method in an 80 L Teflon bag located in a wooden box with the internal walls covered with aluminum foil and operated at (298 ± 1) K and atmospheric pressure (750 ± 10) Torr. The organic reactants were flushed into the bag with a stream of nitrogen. The bag was then filled to its full capacity at atmospheric pressure with nitrogen. Before each set of experiments, the bag was cleaned by filling it with a mixture of O_2 and N_2 photolyzed for 10 min using germicidal lamps (Philips 30 W) with UV emission at 254 nm in order 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. Reaction mixtures consisting of a reference and the sample organic compound, diluted in nitrogen, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h.

For OH reactions: H_2O_2 was used to generate OH radicals by its photolysis using a set of germicidal lamps. These lamps provide UV-radiation with a wavelength maximum around 254 nm. In this work, typically six of these lamps were used to produce OH radicals and the time of photolysis varied from 20 s to 3 min. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a carbowax HP-20M. The column temperature was 35 °C for 11 min at a rate of 20 °C/min to 55 °C for the OH radicals with *(E)*-2-hexenyl acetate. For the reactions of OH radicals with 4-methyl-3-penten-2-one the temperature program was 35 °C when the reference compound was 2-buten-1-ol and 35 °C for 7 min at a rate of 15 °C/min to 50 °C when the reference compound was *(E)*-3-hexen-1-ol. The reference compounds for the OH reactions with *(E)*-2-hexenyl acetate and with 4-methyl-3-penten-2-one were: *(E)*-3-hexen-1-ol $k_{OH} = (1.2 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Gibilisco et al., 2013) and 2-buten-1-ol $k_{OH} = (9.80 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Cometto et al., 2008), respectively.

For Cl reactions: oxalyl chloride (ClC(O)C(O)Cl) was used to generate Cl radicals by its photolysis using a set of germicidal lamps. These lamps provide UV-radiation with a wavelength maximum around 254 nm. In the present work, typically six of these lamps were used to produce Cl radicals and the time of photolysis varied from 5 to 40 s. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID) using a carbowax HP-20M. The column was held at 40 °C for the Cl atoms with *(E)*-2-hexenyl acetate. The temperature program for the reactions of Cl atoms with 4-methyl-3-penten-2-one was 30 °C when the reference was butyl methacrylate and 27 °C when the reference was butyl acrylate. The reference compounds for the Cl reactions with *(E)*-2-hexenyl acetate and with 4-methyl-3-penten-2-one were: *n*-butyl-acrylate $k_{Cl} = (2.50 \pm 0.78) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Blanco et al., 2009a) and *n*-butyl methacrylate $k_{Cl} = (3.60 \pm 0.87) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Blanco et al., 2009b).

The samples were collected using solid phase microextraction technique (SPME). The fiber used was 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/Carboxen/PDMS) from Supelco, Bellefonte, PA, USA. For the kinetic experiments, after 5 min of photolysis the SPME fiber was exposed in the reaction chamber during 10 min. After that, the adsorbed sample was transferred to the GC column keeping the SPME fiber for 2 min in the heated chromatograph injector. The injector temperature was 250 °C for the OH reactions with both studied compounds and for the Cl atoms reaction with *(E)*-2-hexenyl acetate; and 170 °C for the Cl atoms reaction with 4-methyl-3-penten-2-one.

Room temperature products identification experiments were performed using SPME/GC-MS technique. For the OH reactions with the studied compounds, mixture of *(E)*-2-hexenyl acetate/H_2O_2/air and mixture of 4-methyl-3-penten-2-one/H_2O_2/air were flushed into the Teflon bag. For the Cl atoms reactions mixture of *(E)*-2-hexenyl acetate/ClC(O)C(O)Cl/air and mixture of 4-methyl-3-penten-2-one/ClC(O)C(O)Cl/air also were flushed into the Teflon bag. The photolysis time was 30 s for each experiments. In order to identify carbonyl products the *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) derivatizing agent was used. The PFBHA reacts with carbonyl compounds forming a stable oxime. A 2 mL aqueous solution of PFBHA (25 mg/mL) was prepared in a 4 mL vial. The PFBHA was loaded on the SPME fiber during 40 s by head-space extraction. The fiber-PFBHA was exposed inside the chamber other 40 s to produce the oxime on the fiber to be transferred to the GC-MS injector. The desorption time was 2 min at 225 °C. The column employed was Zebron ZB-5MS (30 m × 0.25 mm × 0.25 μm). The temperature program was 80 °C for 3 min, 100 °C for 5 min, 200 °C for 5 min to 250 °C at a rate of 15°/min for the OH radicals and Cl atoms reactions with *(E)*-2-hexenyl acetate. For the OH radicals and Cl atoms reactions with 4-methyl-3-penten-2-one the column temperature was similar to the ester reactions, except that 80 °C was held for 5 min.

The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were: *(E)*-2-hexenyl acetate (235–370); 4-methyl-3-penten-2-one (270–313); *(E)*-3-hexen-1-ol (170–210); 2-buten-1-ol (222–284); *n*-butyl acrylate (222–310); *n*-butyl methacrylate (210–310); oxalyl chloride (164–247) and hydrogen peroxide (150–235).

The purity of the reagents used in this work is as follows: *(E)*-2-hexenyl acetate (Aldrich ≥ 98%); 4-methyl-3-penten-2-one (Aldrich 90%); *(E)*-3-hexen-1-ol (Aldrich 97%); 2-buten-1-ol (Aldrich 96%); *n*-butyl methacrylate (Aldrich 99%); *n*-butyl acrylate (Fluka 99%); hydrogen peroxide (Cicarelli 30%) and oxalyl chloride (Aldrich 99%).

3. Results

Relative rate coefficients for the reactions of OH radicals and Cl atoms with as *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one were determined by comparing the OH and Cl reaction rates with the BVOCs to that with the reference compounds

$$X + \text{BVOC} \rightarrow \text{Products}\ k_{\text{BVOC}} \quad (5)$$

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

where X = OH radical or Cl atom.

Provided that the reaction with OH radicals or Cl atoms is the only significant loss process for both, reactant and reference compounds, it can be shown that:

$$\ln([\text{BVOC}]_0/[\text{BVOC}]_t) = (k_{\text{BVOC}}/k_{\text{Reference}}) \times \ln([\text{Reference}]_0/[\text{Reference}]_t) \quad (\text{I})$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t, respectively. Plots of $\ln([\text{BVOC}]_0/[\text{BVOC}]_t)$ versus $\ln([\text{Reference}]_0/[\text{Reference}]_t)$ should yield straight lines with slope $k_{\text{BVOC}}/k_{\text{Reference}}$.

The mixtures of the BVOCs and references with H_2O_2 and ClC(O)

C(O)Cl were stable in the dark when left in the chamber for about 1 h. Moreover, in the absence of H_2O_2 and ClC(O)C(O)Cl, photolysis of the mixtures (BVOCs and references in air or nitrogen) for more than 1 h shown negligible decrease in the concentrations.

By using this technique, the rate coefficients for the studied reactions were obtained from Equation (I). The data were fitted to a straight line by the linear least-squares procedure. Fig. 1a, b, c and d show the plot of ln ($[BVOC]_0/[BVOC]_t$) versus ln ($[Reference]_0/[Reference]_t$) for the reactions 1, 2, 3 and 4, respectively. For each organic reactant studied, two runs were performed for each reference compounds in order to determinate the rate coefficients which are included in Fig. 1.

The rate coefficients obtained by averaging the values from different experiments in the absolute terms were the following:

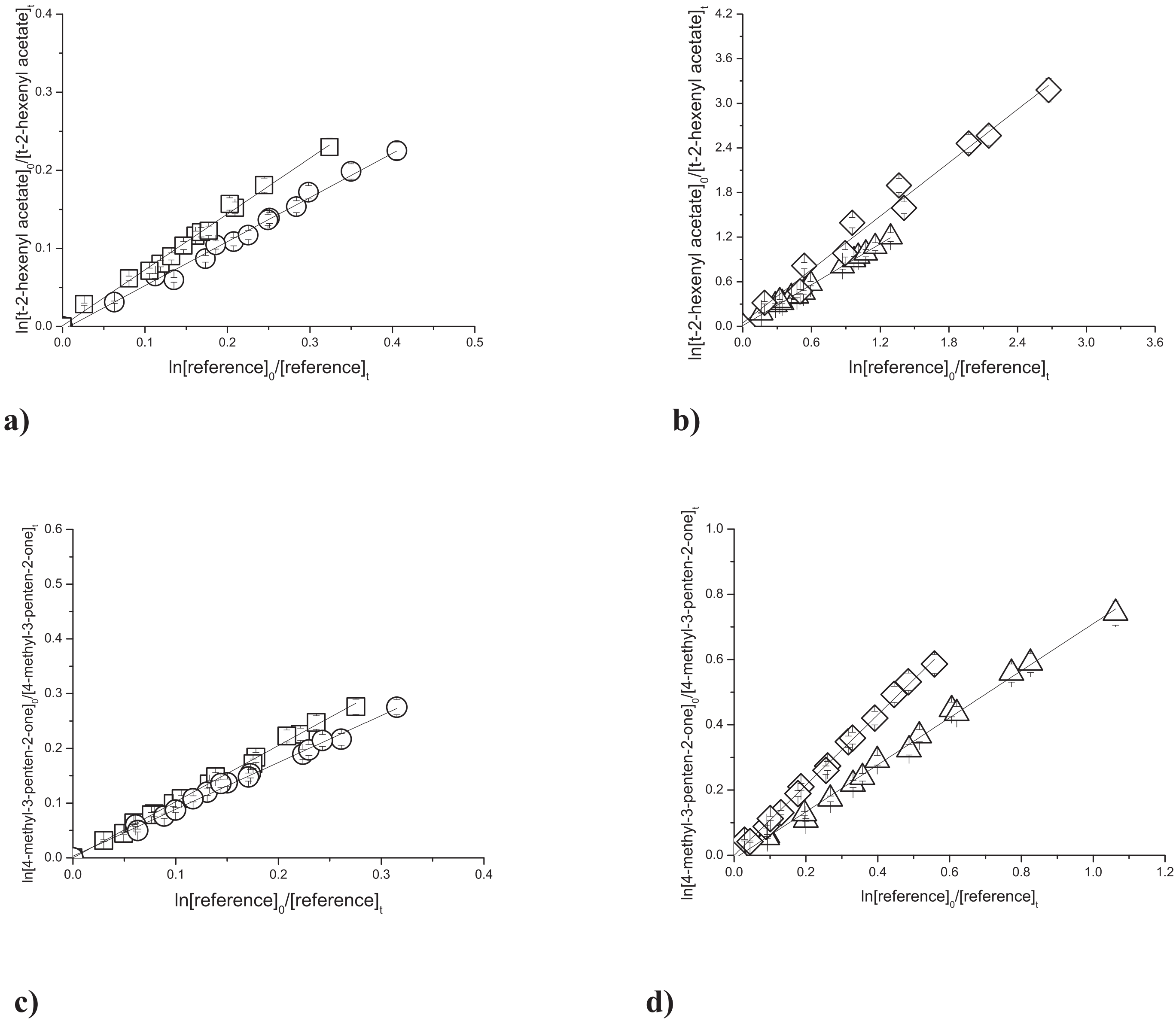
$$k_1 = (6.88 \pm 1.41) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_2 = (3.10 \pm 1.13) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_3 = (1.02 \pm 0.20) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_4 = (2.66 \pm 0.90) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The linearity of the data points and the fact that the plots show practically zero intercepts suggest that secondary reactions are negligible. In Table 1, the rate coefficients ratios are given along with the derived rate coefficients for the OH radical and Cl atom reactions with the BVOCs studied. The uncertainties are a combination of the 2σ statistical errors from the linear regression analysis and a contribution to cover errors in the rate coefficients of the reference compounds. Possible artifacts in the kinetic experiments as product bands that could overlap the reactant and reference bands were negligible in our experimental conditions



a) **b)** **c)** **d)**

Fig. 1. Plot of the kinetic data at 298 ± 1 K and atmospheric pressure of nitrogen for: **a)** the reaction of OH radicals with *(E)*-2-hexenyl acetate measured relative to (○) *(E)*-3-hexen-1-ol and (□) 2-buten-1-ol; **b)** for the reaction of Cl radicals with *(E)*-2-hexenyl acetate measured relative to (Δ) *n*-butyl methacrylate and (◊) *n*-butyl acrylate; **c)** for the reaction of OH radicals with 4-methyl-3-penten-2-one measured relative to (○)*(E)*-3-hexen-1-ol and (□) 2-buten-1-ol and **d)** for the reaction of Cl radicals with 4-methyl-3-penten-2-one measured relative to (Δ) *n*-butyl methacrylate and (◊) *n*-butyl acrylate.

Table 1
Rate coefficient ratios $k_{BVOC}/k_{Reference}$ and absolute rate coefficients for the reactions of OH and Cl radicals with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one at (298 ± 1) K and (750 ± 10) Torr of nitrogen.

Reaction	Reference	$k_{BVOC}/k_{Reference}$	$k_{BVOC} \times 10^{11}$ (cm^3 $molecule^{-1}.s^{-1}$)
(E)-2-hexenyl acetate + OH	*(E)*-3-hexen-1-ol	0.552 ± 0.025	6.62 ± 1.41
	(E)-3-hexen-1-ol	0.564 ± 0.008	6.77 ± 1.23
	2-buten-1-ol	0.718 ± 0.012	7.03 ± 1.20
	2-buten-1-ol	0.722 ± 0.029	7.08 ± 1.37
		average	**6.88 ± 1.41**
Reaction	**Reference**	**$k_{BVOC}/k_{Reference}$**	**$k_{BVOC} \times 10^{10}$ (cm^3 $molecule^{-1}s^{-1}$)**
4-methyl-3-penten-2-one + OH	*(E)*-3-hexen-1-ol	0.839 ± 0.022	1.01 ± 0.19
	(E)-3-hexen-1-ol	0.879 ± 0.022	1.05 ± 0.20
	2-buten-1-ol	1.017 ± 0.012	1.00 ± 0.16
	2-buten-1-ol	1.041 ± 0.021	1.02 ± 0.18
		average	**1.02 ± 0.20**
(E)-2-hexenyl acetate + Cl	*n*-butyl methacrylate	0.844 ± 0.048	3.04 ± 0.91
	n-butyl methacrylate	0.909 ± 0.014	3.27 ± 0.84
	n-butyl acrylate	1.230 ± 0.039	3.07 ± 1.05
	n-butyl acrylate	1.206 ± 0.074	3.02 ± 1.13
		average	**3.10 ± 1.13**
4-methyl-3-penten-2-one + Cl	*n*-butyl methacrylate	0.746 ± 0.021	2.68 ± 0.72
	n-butyl methacrylate	0.711 ± 0.009	2.56 ± 0.65
	n-butyl acrylate	1.083 ± 0.020	2.71 ± 0.90
	n-butyl acrylate	1.074 ± 0.020	2.68 ± 0.89
		average	**2.66 ± 0.90**

(temperature, gases flow in the GC and degree of conversion of the reactions studied).

In addition, product experiments were performed to identify the reaction products formed for the reactions of OH radicals and Cl atoms with the BVOCs studied in the absence of NO_x.

Butanal was positively identified for the reactions of OH radicals with *(E)*-2-hexenyl acetate (see Fig. 4a). Acetone and formaldehyde were identified as reaction products for the OH + 4-methyl-3-penten-2-one reaction (see Fig. 4b and c).

On the other hand, formaldehyde was observed for the Cl-initiated reaction of *(E)*-2-hexenyl acetate and acetone together with formaldehyde were observed in the Cl + 4-methyl-3-penten-2-one reaction. The identified products formaldehyde, acetone and butanal react with the derivatizing agent forming formaldoxime (MW = 225), acetoneketoxime (MW = 253) and *n*-butyraldoxime (MW = 267), respectively.

4. Discussion

The present study is the first experimental measurement of the rate coefficients of the reactions (1)–(4) and therefore no direct comparison with previous determinations can be made. However, the rate coefficient for the reaction of OH with 4-methyl-3-penten-2-one was estimated by Grosjean and Williams (1992) using structure-reactivity and linear free-energy relationships (SRR). The authors have reported an estimated value of 5.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for this reaction which is approximately 50% lower to the experimental value reported in this work of $(10.2 \pm 2.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

The structure-activity relationship (SAR) method of Kwok and Atkinson for OH reactions (Kwok and Atkinson, 1995) gives values (in units of cm^3 $molecule^{-1}$ s^{-1}) of 6.80×10^{-11} and 0.79×10^{-10} for the reactions of OH with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one, respectively which are in very good agreement with the values of $k_1 = (6.88 \pm 1.41) \times 10^{-11}$ and $k_3 = (1.02 \pm 0.20) \times 10^{-10}$ reported in this work for these reactions. Give even the same reactivity trend for the reactions determined in this work:

$$k_{1((E)\text{-2-hexenyl acetate+OH})} < k_{3(\text{4-methyl-3-penten-2-one+OH})}$$

These estimated values are slightly lower than those obtained experimentally but in very good agreement within experimental errors reported in this work.

Additionally, the rate coefficients obtained can be compared with values calculated using the reported correlation between the reactivity of the VOC toward OH radicals and Cl atoms with the Highest Occupied Molecular Orbital (HOMO) of the unsaturated compounds (Blanco et al., 2009b).

The correlations obtained in our previous study (Blanco et al., 2009b) for different groups of reactions are as follows:

$$\ln k_{OH}\ (cm^3\ molecule^{-1}\ s^{-1}) = -(1.1 \pm 0.2)\ E_{HOMO} - (12.6 \pm 1.7) \quad (II)$$

$$\ln k_{Cl}\ (cm^3\ molecule^{-1}\ s^{-1}) = -(0.1 \pm 0.1)\ E_{HOMO} - (21.2 \pm 2.9) \quad (III)$$

We have calculated the HOMO energies for the BVOCs studied using the Gaussian 03 package. 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 calculated by Moller–Plesset perturbation theory (MP4-SCF) using an “ab initio” Hamiltonian with a 6–311++ G (d,p) bases set.

The values of E_{HOMO} of 9.86 eV for *(E)*-2-hexenyl acetate and 9.74 eV for 4-methyl-3-penten-2-one, were used to obtain the following rate coefficients: $k_{1(\text{t-2-hexenyl acetate+OH})} = 6.57 \times 10^{-11} cm^3$ $molecule^{-1}$ s^{-1} and $k_{3(\text{4-methyl-3-penten-2-one+OH})} = 7.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} through Equation II and $k_{2((E)\text{-2-hexenyl acetate+Cl})} = 2.31 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{4(\text{4-methyl-3-penten-2-one+Cl})} = 2.34 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} from Equation III, respectively. These values agree very well with the rate coefficient of reactions 1–4 measured in this study of 6.88×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, 3.10×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, 1.02×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and 2.66×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively.

In the terms of frontier molecular orbital theory, the energy difference between the highest occupied molecular orbital (HOMO) of the unsaturated VOC and the singly occupied molecular orbital (SOMO) for the OH/Cl oxidant can be linearly related to the activation barrier for the addition reaction that form the unsaturated VOC-OH/Cl adduct. Therefore, the logarithm of the rate coefficient for the reaction is expected to be linearly related to the HOMO and SOMO energy gap. As the energy of the singly occupied molecular orbital is the same for OH/Cl oxidant in E_{SOMO}, the logarithm of the rate coefficient will also simply be linearly related to the energy of the HOMO of the unsaturated VOC.

4.1. Reactivity trends

It is interesting to compare the rate coefficient values reported in this work with the available literature data for the reactions of other unsaturated VOCs with OH radicals and Cl atoms (see Table 2).

The rate coefficients for the reactions of OH radicals with the unsaturated acetates are within (2.48–7.84) × 10^{-11} cm^3 molecule^{-1} s^{-1} (Table 2). We can observe the increase of the rate coefficients due to the presence of alkyl groups ($-CH_2-$, CH_3-) in the unsaturated ester. In this sense, we can observe from Table 2 that the rate coefficient for the reaction of OH with vinyl acetate ($CH_3C(O)OCH{=}CH_2$) is lower than the rate coefficient for the reaction of OH with allyl acetate ($CH_3C(O)OCH_2CH{=}CH_2$) due to the addition of a $-CH_2-$ group in allyl acetate:

$k_{(OH+CH3C(O)OCH=CH2)}$: 2.48 × 10^{-11} cm^3 molecule^{-1} s^{-1} < $k_{(OH+CH3C(O)OCH2CH=CH2)}$: 3.06 × 10^{-11} cm^3 molecule^{-1} s^{-1}.

If in allyl acetate we replace a hydrogen atom of the terminal carbon of the double bond by a propyl group forming *(E)*-2-hexenyl acetate, the OH rate coefficient increase more than 2 times.

$k_{(OH+CH3C(O)OCH2CH=CH2)}$: 3.06 × 10^{-11} cm^3 molecule^{-1} s^{-1} < $k_{(OH+CH3C(O)OCH2CH=CHCH2CH2CH3)}$: 6.88 × 10^{-11} cm^3 molecule^{-1} s^{-1}.

This change in the reactivity could be attributed to the positive inductive effect of the alkyl groups that increases the charge density on the double bond (>C=C<) and consequently the rate coefficient value of the reaction. This behavior is indicative of an electrophilic addition mechanism.

In addition, if a $-CH_2-$ entity of propyl group in *(E)*-2-hexenyl acetate is now located next to the carbon atom of the double bond closest to the carbonyl group forming *(Z)*-3-hexenyl-acetate ($CH_3C(O)OCH_2CH_2CH{=}CHCH_2CH_3$) the OH rate coefficient value increases:

$k_{(OH+CH3C(O)OCH2CH=CHCH2CH2CH3)}$: 6.88 × 10^{-11} cm^3 molecule^{-1} s^{-1} < $k_{(OH+ CH3C(O)OCH2CH2CH=CHCH2CH3)}$: 7.84 × 10^{-11} cm^3 molecule^{-1} s^{-1}.

Although, in this case, the position of the alkyl substituent varied in the ester chain keeping the number of -CH_2 groups in the molecule. The larger distance between the double bond and the ester group could have an influence in the increase of the rate coefficient of OH with *(Z)*-3-hexenyl-acetate than OH+ *(E)*-2-hexenyl acetate rate coefficient value.

The kinetic data base on the reactions of atmospheric oxidants with unsaturated ketones (Calvert et al., 2011; NIST Chemical Kinetics Database) is limited. We have reported a previous kinetic study for the reactions of OH radicals and Cl atoms with α-unsaturated ketones (5-hexen-3-one, 3-penten-2-one and 4-hexen-3-one) performed in a 480 L glass chamber. In that work, we have observed that the rate coefficients for the reactions of OH radicals with α-unsaturated ketones are either similar or higher than those of the corresponding alkenes (Blanco et al., 2012). As we have observed in the OH reactions of other carbonyl compounds as unsaturated esters (Teruel et al., 2006), it is expected that the OH rate coefficients for all of the α,β-unsaturated ketones investigated are lower than those of their analogous alkenes based on the deactivating effect of the $-C(O)-$ group toward electrophilic reactions. For the reaction of 4-methyl-3-penten-2-one with OH the rate coefficient value (10.2 × 10^{-11} cm^3 molecule^{-1} s^{-1}) is higher than the rate coefficient value of the parent alkene ($(CH_3)_2C{=}CHCH_2CH_3$) with OH radicals of 8.75 × 10^{-11} cm^3 molecule^{-1} s^{-1} (NIST Chemical Kinetics Database). This behavior was rationalized considering that the reactions of OH with the unsaturated ketones proceed via a mechanism involving a hydrogen bonded complex between the OH radical and the carbonyl group (Blanco et al., 2012).

Table 2

Comparison of the rate coefficient values for the reaction of OH radicals and Cl atoms with a series of unsaturated esters (acetates) and unsaturated ketones at 298 K and atmospheric pressure.

VOC	$k_{OH} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	$k_{Cl} \times 10^{10}$ (cm^3 molecule^{-1} s^{-1})
Unsaturated Esters		
$CH_3C(O)OCH{=}CH_2$	(2.48 ± 0.61)[a]	(2.68 ± 0.91)[g]
$CH_3C(O)OCH_2CH{=}CH_2$	(3.06 ± 0.31)[b]	(1.30 ± 0.45)[g]
$CH_3C(O)OCH_2CH{=}CHCH_2CH_2CH_3$	(6.88 ± 1.41)[c]	(3.10 ± 1.13)[c]
$CH_3C(O)OCH_2CH_2CH{=}CHCH_2CH_3$	(7.84 ± 1.64)[d]	–
Unsaturated Ketones		
$CH_3C(O)C(CH_3){=}CH_2$	3.60[e]	(2.38 ± 0.26)[h]
$CH_3CH{=}C(CH_3)C(O)CH_3$	4.20[e]	(3.00 ± 0.34)[h]
$CH_2{=}CHCH_2CH_2C(O)CH_3$	(5.18 ± 1.27)[f]	(3.15 ± 0.50) [f]
$CH_3C(O)CH{=}CHCH_3$	(7.22 ± 1.74)[f]	(2.53 ± 0.54) [f]
$CH_3CH_2C(O)CH{=}CHCH_3$	(9.04 ± 2.12)[f]	(3.00 ± 0.58) [f]
$(CH_3)_2C{=}CHC(O)CH_3$	(10.2 ± 2.00)[c]	(2.66 ± 0.90)[c]

[a] Blanco et al., 2009c.
[b] Picquet-Varrault et al., 2002.
[c] This work.
[d] Atkinson et al., 1995.
[e] Grosjean and Williams, 1992.
[f] Blanco et al., 2012.
[g] Blanco et al., 2009a.
[h] Wang et al., 2015.

A similar tendency has been discussed previously for reactions of OH radicals with other oxygenated organics (Mellouki et al., 2003). As we have observed in the reactions of OH radicals with the unsaturated esters, the reactions of OH radicals with unsaturated ketones show an increase in reactivity towards electrophilic attack by OH radical with increasing methyl substitution at the double bond due the positive inductive effect of these electron density donating groups (see Table 2).

Table 2 shows that the unsaturated esters and ketones are more reactive toward Cl atoms than OH radicals and also the effect of the alkyl substituents on the reactivity of the double bond is less important in Cl reactions than in OH reactions. This is due to the rate coefficients of the Cl atoms with the unsaturated carbonyl compounds are close to the gas kinetic limited value from the gas collision theory (Blanco et al., 2009a, 2009b).

4.2. *Product identification*

The products identified in this work together with the reactivity trends of these compounds suggest that the reactions of OH radicals and Cl atoms with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one mainly lead to the formation of hydroxy/chloro alkyl radicals by initial addition of OH/Cl radicals to the double bond. The hydroxy/chloro alkyl radicals rapidly react with O_2 forming hydroxy/chloro alkyl peroxy radicals. Further, hydroxy/chloro peroxy radicals react with other peroxy radicals (in the absence of NO_x) to give the hydroxy/chloro alkoxy radicals.

The hydroxy/chloro alkoxy radicals formed could be $CH_3C(O)OCH_2C(X)C(O^{\bullet})CH_2CH_2CH_3$ and $CH_3C(O)OCH_2C(O^{\bullet})C(X)CH_2CH_2CH_3$ for the reaction of *(E)*-2-hexenyl acetate + OH and $CH_3C(O)CH(X)C(O^{\bullet})(CH_3)_2$ and $CH_3C(O)CH(O^{\bullet})C(X)(CH_3)_2$ for the reaction of 4-methyl-3-penten-2-one + OH, where X = OH or Cl.

A postulated mechanism for the reactions of OH radicals/Cl atoms with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one in the absence of NO_x is shown in Fig. 2a, b and 3a, b, respectively.

4.2.1. *(E)-2-hexenyl acetate*

The addition of OH radicals and Cl atoms can be in the C4 to lead $CH_3C(O)OCH_2C(X)C(O^{\bullet})CH_2CH_2CH_3$ radicals (Fig. 2a) and/or in the C5 to produce $CH_3C(O)OCH_2C(O^{\bullet})C(X)CH_2CH_2CH_3$ radicals (Fig. 2b).

For both reactions studied, the hydroxyl/chloro alkoxy radicals formed in the OH/Cl addition step (Fig. 2a and b), can:

a) decompose to give butanal ($HC(O)CH_2CH_2CH_3$) and $CH_3C(O)OCH_2CH^{\bullet}(OH)/CH_3C(O)OCH_2CH^{\bullet}(Cl)$ radical. (Fig. 2a, channel A) for the OH/Cl-addition in C4, or $HC(O)CH(OH)CH_2CH_2CH_3/HC(O)CH(Cl)CH_2CH_2CH_3$ and $CH_3C(O)OCH_2^{\bullet}$ radical that after oxidation could form $CH_3C(O)OC(O)H$ (Fig. 2b, channel A) for the OH/Cl-addition in C5.
b) decompose to give $CH_3C(O)OCH_2CH(OH)C(O)H/CH_3C(O)OCH_2CH(Cl)C(O)H$ and $CH_3CH_2CH_2^{\bullet}$ with further production of formaldehyde and/or propanal (Fig. 2a, channel B) for the OH/Cl-addition in C4, or $CH_3C(O)OCH_2C(O)H$ and $CH_3CH_2CH_2CH(OH)/CH_3CH_2CH_2CH(Cl)$ radical with further formation of $CH_3CH_2CH_2C(O)OH/CH_3CH_2CH_2C(O)Cl$ (Fig. 2b, channel B) for the OH/Cl-addition in C5.
c) react with O_2 to form a polyfunctional compound, $CH_3C(O)OCH_2CH(OH)C(O)CH_2CH_2CH_3/CH_3C(O)OCH_2CH(Cl)C(O)CH_2CH_2CH_3$ and hydroperoxy radical (Fig. 2a, channel C) for the OH/Cl-addition in C4.
d) react with O_2 to form $CH_3C(O)OCH_2C(O)CH(OH)CH_2CH_2CH_3/CH_3C(O)OCH_2C(O)CH(Cl)CH_2CH_2CH_3$ and hydroperoxy radical if the OH/Cl-addition is produced in C5 (Fig. 2b, channel C).

4.2.2. *4-methyl-3-penten-2-one*

For the reaction of 4-methyl-3-penten-2-one the addition of OH radical/Cl atom to the double bond could be produced in the carbon 3 or 4 of the >C=C< (Fig. 3a, b). The alkoxy radicals formed can:

a) decompose to produce acetone ($CH_3C(O)CH_3$) and $CH_3C(O)CH(OH)^{\bullet}/CH_3C(O)CH(Cl)$ radicals if the addition occurs in the C3 of the double bond (Fig. 3a, channel A). When the addition of OH/Cl radical is located in the C4 of the double bond, methyl glyoxal ($CH_3C(O)C(O)H$) and $^{\bullet}C(CH_3)_2(OH)/{}^{\bullet}C(CH_3)_2(Cl)$ radical could be produced. The $^{\bullet}C(CH_3)_2(OH)$ radical formed in the OH reactions can react further with O_2 forming acetone and $^{\bullet}HO_2$ radicals. In the Cl atom addition, the $^{\bullet}C(CH_3)_2(Cl)$ radical formed can react further with O_2 in the presence of $RO_2^{\bullet}$ radicals followed by an ejection of Cl atom to form acetone (Fig. 3b, channel A),
b) decompose forming $CH_3C(O)CH(OH)C(O)CH_3/CH_3C(O)CH(Cl)C(O)CH_3$ and $CH_3^{\bullet}$ radical with further production of formaldehyde (Fig. 3a, channel B) for the OH/Cl-addition in C3.
c) decompose forming $HC(O)C(CH_3)_2(OH)/HC(O)C(CH_3)_2(Cl)$ and $CH_3C(O)^{\bullet}$ radical which can react further with O_2 in the presence of $RO_2^{\bullet}$ radicals followed by a decomposition to give CO_2 and $^{\bullet}CH_3$ radical and further production formation of formaldehyde when the OH/Cl addition occurs in the carbon 4 of the double bond (Fig. 3b, channel B).
d) react with O_2 to form a polyfunctional compound $CH_3C(O)C(O)C(CH_3)_2OH/CH_3C(O)C(O)C(CH_3)_2Cl$ and hydroperoxy radical only if the OH/Cl addition is produced in the carbon 4 of the double bond (Fig. 3b channel C).

In our experimental conditions and using the derivatizing agent *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) to monitor carbonyl compounds, we have observed the presence of butanal in the reaction of OH radicals with *(E)*-2-hexenyl acetate. This product can be formed through the addition of OH radical to the carbon 4 of the double bond (Fig. 2a) followed by the decomposition pathway (Fig. 2a channel A). CG-MS experiments have shown butanal as the main product (with fragments of *m/z* 267 (for (syn) *n*-butyraldoxime and (anti)*n*-butyraldoxime) 181 and 86 characteristic of this kind of compound). An example of the chromatogram obtained for the butanal formation in the OH reaction is showed in Fig. 4a.

For the Cl + *(E)*-2-hexenyl acetate reaction the presence of formaldehyde was observed with fragments of *m/z* 225 (for formaldoxime), 181 and 44. Formaldehyde is a co-product of $CH_3C(O)OCH_2CH(Cl)C(O)H$ and could be formed trough the decomposition of the chloroalkoxy radical formed, Fig. 2a, channel B. The presence of $CH_3C(O)OCH_2CH(Cl)C(O)H$ was not observed in our experimental conditions, neither butanal in the reaction of Cl atoms with *(E)*-2-hexenyl acetate.

For the reactions of OH radicals and Cl atoms with 4-methyl-3-penten-2-one, acetone and formaldehyde were observed as products for both reactions with ions with *m/z* = 253 (for acetoneketoxime), 181 and 72; and 225 (for formaldoxime), 181 and 44, respectively.

Acetone formation observed could be explained through the decomposition of the hydroxy/chloro alkoxy radical formed when OH/Cl radical is added in the carbon 3 of the double bond (Fig. 3a, channel A). The formation of formaldehyde could be attributed to the decomposition of this hydroxy/chloro alkoxy radical (Fig. 3a, channel B). However, acetone and formaldehyde could be also formed when the addition of OH/Cl radical is located in the carbon 4 of the >C=C< trough the decomposition of the hydroxy/chloro alkoxy radical formed (Fig. 3b) by channels A and B, respectively. An example of chromatogram for the acetone formation in the OH

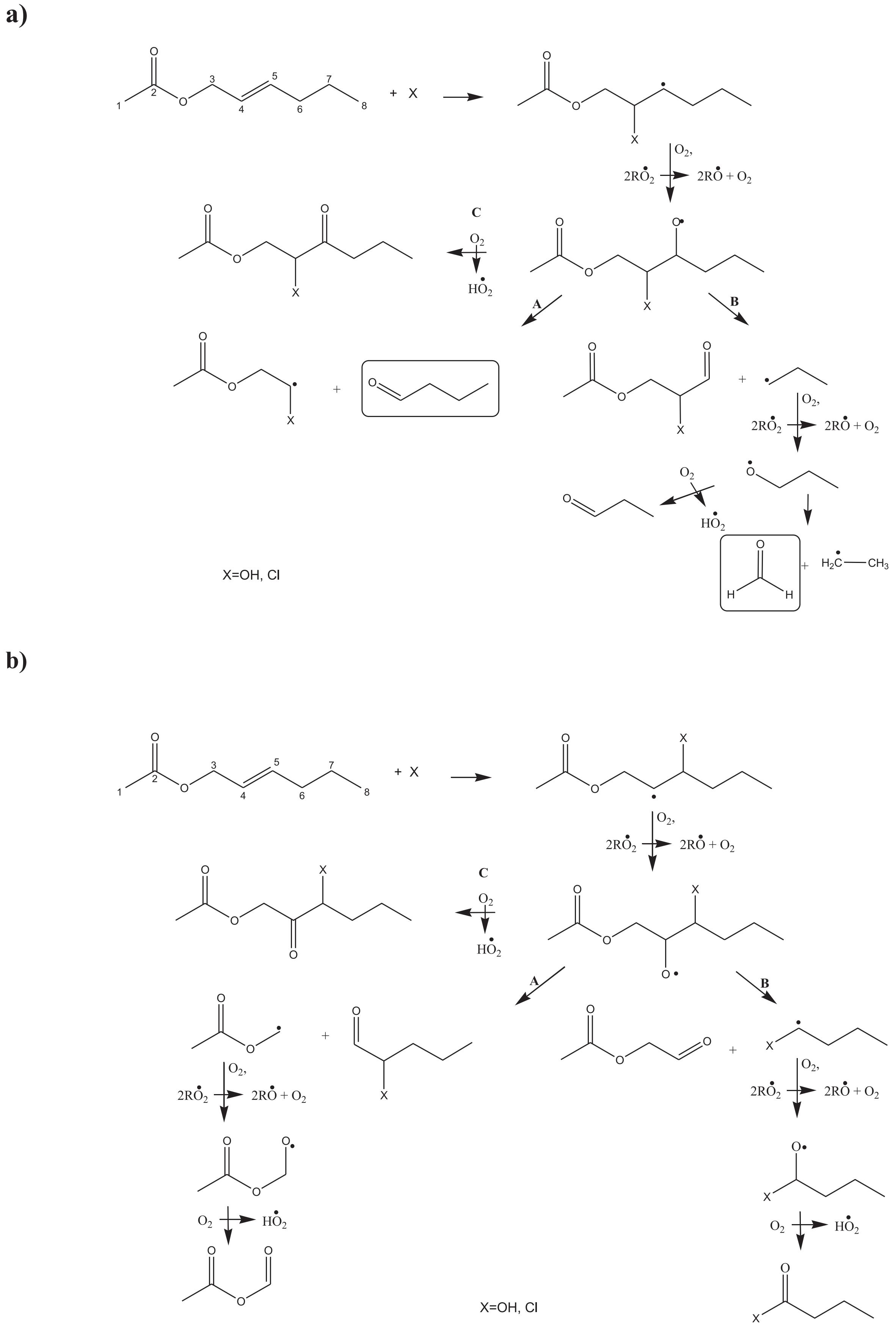


Fig. 2. Simplified mechanism for the OH radical/Cl atom initiated oxidation of *(E)*-2-hexenyl acetate. a) Via addition of OH/Cl to the carbon 4 of the double bond. b) Vía addition of OH/Cl to the carbon 5 of the double bond. The identified products are showed in filled line.

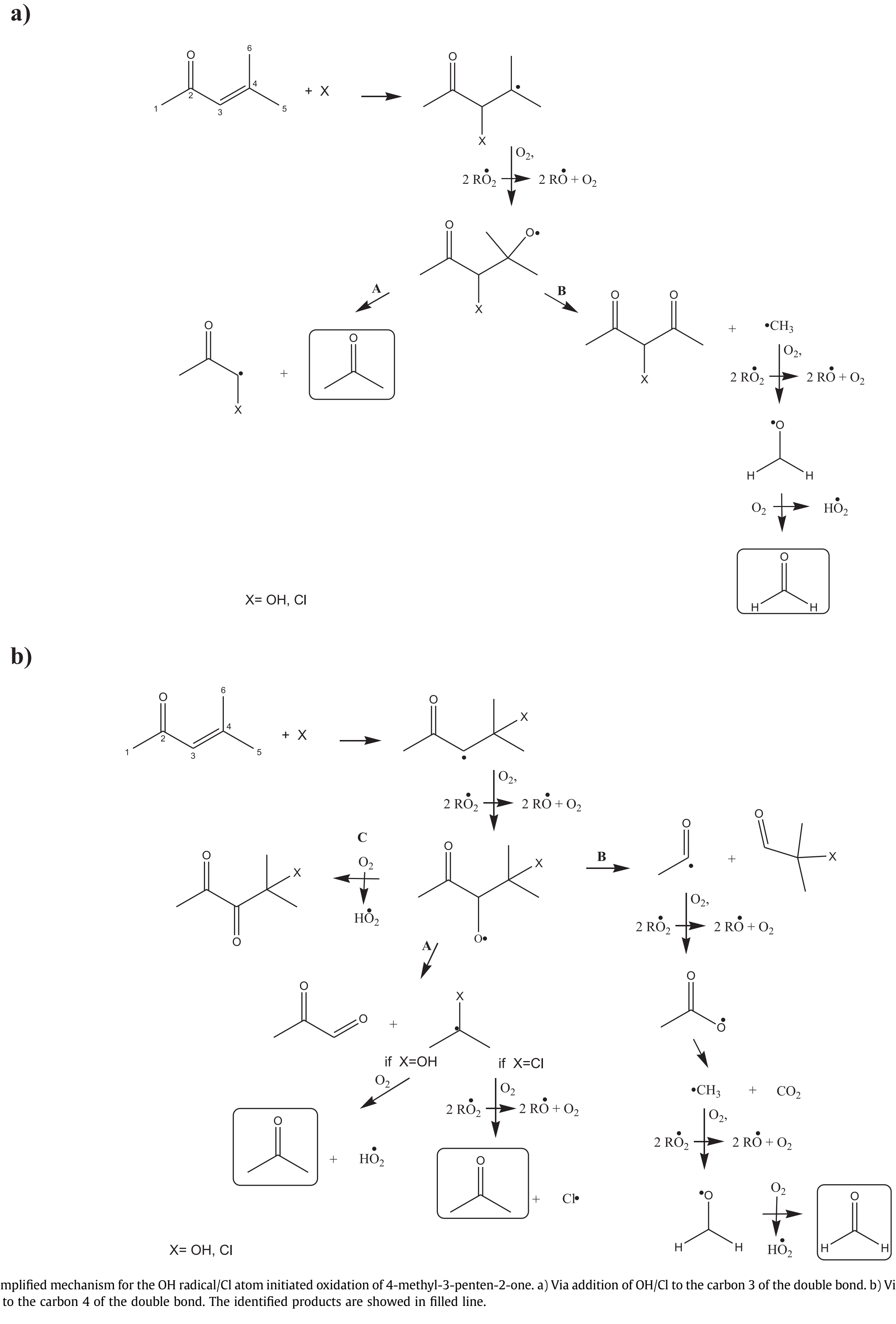


Fig. 3. Simplified mechanism for the OH radical/Cl atom initiated oxidation of 4-methyl-3-penten-2-one. a) Via addition of OH/Cl to the carbon 3 of the double bond. b) Via addition of OH/Cl to the carbon 4 of the double bond. The identified products are showed in filled line.

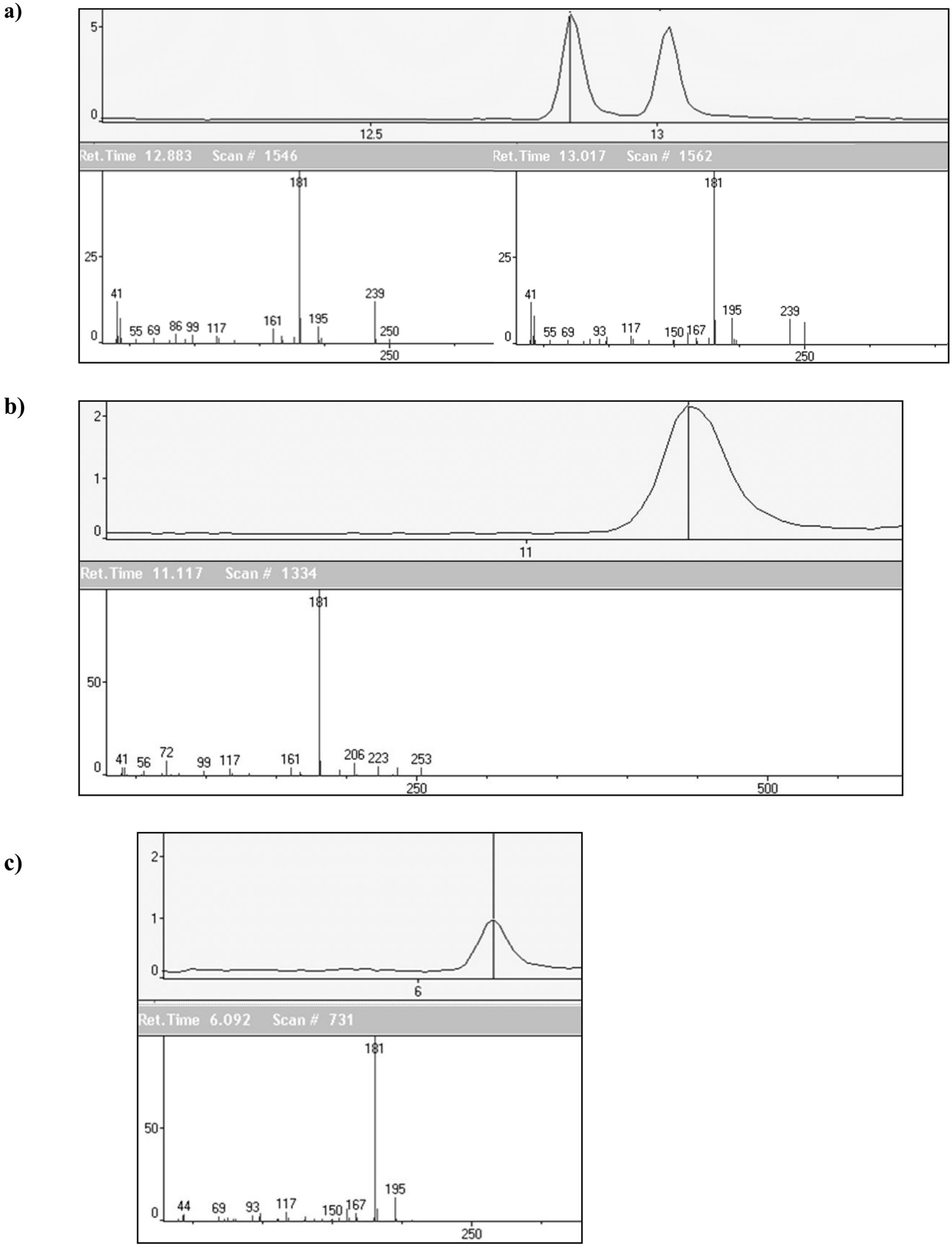


Fig. 4. Example of GC-MS chromatogram of a mixture of *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one with H_2O_2 in air at 298 K and atmospheric pressure.
a) Butyraldoxime chromatogram obtained after photolysis of the mixture of *(E)*-2-hexenyl acetate/H_2O_2/air (Retention time 12.883 and 13.017 min).
b) Acetoneketoxime chromatogram obtained after photolysis of the mixture of 4-methyl-3-penten-2-one/H_2O_2/air (Retention time 11.117 min).
c) Formaldoxime chromatogram obtained after photolysis of the mixture of 4-methyl-3-penten-2-one/H_2O_2/air (Retention time 6.092 min).

reaction is showed in Fig. 4b.

We expect that OH -addition to the carbon 4 of the double bond will be the main pathway in the reactions of OH radicals with *(E)*-2-hexenyl acetate to form butanal (Fig. 2a, channel A). According to the products observed in this work for the Cl+*(E)*-2-hexenyl acetate reaction, the main reaction pathway seems to be the decomposition of the chloroalkoxy radical formed, Fig. 2a, channel B to form $CH_3C(O)OCH_2CH(Cl)C(O)H$ and formaldehyde as a co-product.

The OH/Cl addition to the carbon 3 of the double bond for reaction of OH/Cl radical with 4-methyl-3-penten-2-one forming acetone and formaldehyde could be the main reaction pathway for these reactions. Since, through the OH/Cl radical addition to the carbon 3 in 4-methyl-3-penten-2-one structure is formed a tertiary radical and based on the observed products, acetone is formed directly by decomposition of the alkoxy radical (channel A, Fig. 3a) and formaldehyde through the decomposition of the alkoxy radical and subsequence reaction with O_2 (channel B, Fig. 3a).

4.3. Atmospheric implications

The rate coefficients reported in Table 1 can be used to calculate the atmospheric lifetimes of the unsaturated compounds studied due to reaction with OH radicals and Cl atoms in comparison to their reactions with the other atmospheric oxidants NO_3 radicals and O_3 molecules using the following expression: $\tau_x = 1/k_x[X]$ with X = OH, Cl, NO_3, or O_3, where k_x is the rate coefficient for the reaction of the oxidant X with the unsaturated VOC and [X] is the typical atmospheric concentration of the oxidant. For the calculations, the following oxidant concentrations have been used: $[OH] = 2 \times 10^6$ radicals cm^{-3} (Hein et al., 1997); $[Cl] = 1 \times 10^4$ atoms cm^{-3} (Wingenter et al., 1996); $[NO_3] = 5 \times 10^8$ radicals cm^{-3} (Shu and Atkinson, 1995); and $[O_3] = 7 \times 10^{11}$ molecules cm^{-3} (Logan, 1985). The estimated tropospheric lifetimes at room temperature of the unsaturated compounds with the tropospheric oxidants (where data are available) are presented in Table 3. Due to these BVOCs are photolytically stable in the actinic region of the electromagnetic spectrum we can expect that the photolytic loss of these compounds will be negligible. The lifetimes indicate that these unsaturated VOCs are likely to be removed rapidly (in the order of 1.4–3.9 h by the reaction with OH during the day and NO_3 radicals during the night. Unfortunately, no kinetic data are available on the reactions of NO_3 radicals with *(E)*-2-hexenyl acetate, although, on the basis of chemical structure of the molecule, we would predict that the atmospheric lifetime of *(E)*-2-hexenyl acetate by their reaction with NO_3 will be in the range of a few hours implying that the unsaturated VOCs are likely to be removed rapidly in the gas phase close to their source of emission with removal by OH radicals dominating. The atmospheric lifetimes of these BVOCs regarding to the reaction with O_3 molecules are approximately from 18 to 48 h. However, in polluted areas, where peak concentrations of O_3 around 1×10^{13} molecule cm^{-3} can occur (Seinfeld and Pandis, 1998), O_3-initiated degradation of *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one can be a significant homogeneous loss process.

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

BVOCs	$^a\tau_{OH}$ (hours)	$^a\tau_{Cl}$ (hours)	τ_{O3} (hours)	τ_{NO3} (hours)
(E)-2-hexenyl acetate	2	89.6	18.2[b]	–
4-methyl-3-penten-2-one	1.4	104.4	48[c]	3.9[d]

With $\tau = 1/(k_X [X])$, where X = OH/Cl/O_3/NO_3.

[a] This work.

[b] Grosjean et al., 1996.

[c] Sato et al., 2004.

[d] Canosa-Mas et al., 2005.

The Cl reaction lifetime estimated values are between 89 and 105 h. However, in marine and industrialised continental regions, where high chlorine concentrations can occur especially at dawn with peaks of concentration around 1×10^5 atoms/cm^3 (Spicer et al., 1998), Cl-mediated degradation of the compounds may be able to compete with the OH-initiated oxidation with lifetimes around 9–10 h for the BVOCs studied.

Aldehydes as butanal and formaldehyde were observed as products formed in the reactions of OH/Cl with *(E)*-2-hexenyl acetate and 4-methyl-3-penten-2-one, respectively. These aldehydes will be subject to further reaction with OH/Cl and also photolysis. Formaldehyde is one the most reactive and important species in tropospheric photochemistry and in ozone formation (Calvert et al., 2011). On the other hand, acetone was also observed in the reactions of OH/Cl with 4-methyl-3-penten-2-one.

VOCs containing groups with two methyl as substituents units $(CH_3)_2CH$-, $(CH_3)_2C$=, and $(CH_3)_3C$- will be propensity to form acetone during their photooxidation. There is little information about the acetone formation of these groups units when they are attached directly to an oxygen-containing functionality, i.e. a ketone, ether, alcohol or ester group. We have observed the formation of acetone in the reactions of OH and Cl when the $(CH_3)_2C<$ entity is attached to the carbonyl group. The formation of acetone in the oxidation of VOCs is very important since the photolysis and oxidation of acetone is a source of, peroxy and alkoxy radicals and peroxyacetylnitrate (PAN), a key reservoir for nitrogen oxides ($NO_x = NO + NO_2$) in the free troposphere (Singh et al., 1994; Singh et al., 1995) and in consequence plays an important role in determining the oxidative capacity of the atmosphere (Arnold et al., 1997; Folkins and Chatfield, 2000).

However, more experimental data (products yields in the presence and in the absence of NO_x) and theoretical calculations using different approaches on the mechanisms probably are needed in order to have a better understanding and to confirm the degradation chemistry of these non terminal unsaturated VOCs in the troposphere in order to increase the mechanistic and product data base for the reactions of OH radicals and Cl atoms with unsaturated esters and ketones at room temperature.

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