Relative rate coefficient measurements of OH radical reactions with (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol under simulated atmospheric conditions

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Silvina A. Peirone, Javier A. Barrera, Raúl A. Taccone, Pablo M. Cometto, Silvia I. Lane[*]

Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), CONICET, Centro Láser de Ciencias Moleculares, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

HIGHLIGHTS

- Reaction rate coefficients for OH radicals with two hexenols were determined.
- Atmospheric lifetimes of (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol were estimated.
- GWP calculations for (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol were performed.
- Atmospheric implications of the alcohols emissions briefly discussed.

ARTICLE INFO

ABSTRACT

The relative rate technique was used to determine the rate coefficients of the reactions of OH radicals with (Z)-2-hexen-1-ol (k_1), and (E)-3-hexen-1-ol (k_2), at (296 ± 2) K and (750 ± 10) Torr of N_2 or pure air. The reactions were investigated using a 200 L Teflon reaction chamber and a gas chromatograph coupled with flame-ionization detection. The following rate coefficients were derived, in units of $cm^3\ mol^{-1}\ s^{-1}$: $k_1 = (1.1 \pm 0.4) \times 10^{-10}$ and $k_2 = (0.8 \pm 0.1) \times 10^{-10}$. This is the first experimental determination of k_1 and k_2. A comparison between the experimental rate coefficients (k_{exp}) and the calculated rate coefficients using the structure–activity relationship (SAR) method (k_{SAR}), for the reaction of different unsaturated alcohols with OH radicals is presented. The atmospheric lifetimes of the studied alcohols were estimated considering the rate coefficients of their reactions with OH and NO_3 radicals. The radiative efficiencies (REs) were obtained from the infrared spectra of the two hexenols and the global warming potentials (GWPs) were then estimated. Atmospheric implications of the alcohols emission are briefly discussed.

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1. Introduction

Biogenic volatile organic compounds (BVOCs) emitted from plants are a significant part of the total amount of organic compounds present in the atmosphere. These emissions occur during growth, injury and decay of plants. Globally, the BVOCs emissions are around 86% of the total of the volatile organic compounds (VOCs) emitted, while the rest proceed from anthropogenic sources (Guenther et al., 1995). BVOC emissions in North America are dominated by isoprene (51%), terpenes (31%), and oxygenated VOCs (16%), based on hydroxyl radical (OH) reactivity (Guenther et al., 2000).

Emissions of hexenals, hexenols, acetaldehyde, acetone, isoprene and monoterpenes were found from grass cutting (Kirstine et al.,

1998). These emissions are more significant than those produced by undistured pasture. Kirstine and Galbally (2004), calculated that the C6 compounds produced by the cutting of grasses could contribute with 3–5% of the total urban VOCs emissions.

Hence, the biogenic compounds are chemically active in the atmosphere and their gas-phase chemistry has a direct impact on air quality on local to regional scales through their impact on the abundance of OH radicals, ozone production, and contributions to secondary organic aerosol formation.

(Z)-2-hexen-1-ol has been reported as an emission from clipped clover (Kirstine et al., 1998) and is found in abundance in grape leaves and in grape berries (Watkins and Wijesundera, 2006). Emissions of (E)-3-hexen-1-ol have been frequently shown to accompany emissions of the "leaf alcohols", as one of the main volatile fractions from fresh and dry leaves such as those from olive trees (Brahmi et al., 2012). In two sites in the continental USA, the
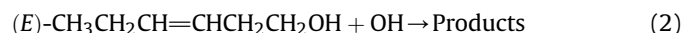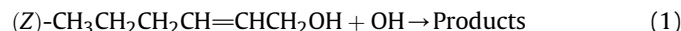
landscape flux potential of (E)-3-hexen-1-ol has been found to be 0.3% of the total VOC flux potential (Helming et al., 1999).

It is, therefore, important to know not only the atmospheric abundance of the biogenic volatile organic compounds, but also their reaction rates and degradation pathways to enable accurate model calculations used for air quality forecasts as well as for regulatory purposes.

Previous laboratory studies have demonstrated that unsaturated alcohols are mainly removed from the atmosphere by reaction with the tropospheric oxidants (OH and NO$_3$ radicals, Cl atoms and O$_3$ molecule) (Finlayson-Pitts and Pitts, 2000), leading to the formation of oxygenated degradation products (Reisen et al., 2003; Aschmann et al., 1997).

In this study, gas-phase rate coefficients were obtained for the reactions of (Z)-2-hexen-1-ol (HxO21) and (E)-3-hexen-1-ol (HxO31) with the OH radical at 298 K and atmospheric pressure. To the best of our knowledge, the only previous kinetic studies of the reactions of these hexenols are with NO$_3$ radicals (Pfang et al., 2006; Zhao et al., 2011). The studied reactions can be schematically written as:

$$(Z)\text{-}CH_3CH_2CH_2CH=CHCH_2OH + OH \rightarrow Products \quad (1)$$

$$(E)\text{-}CH_3CH_2CH=CHCH_2CH_2OH + OH \rightarrow Products \quad (2)$$

The kinetic results obtained will be presented and compared with other similar unsaturated alcohols, taken from the literature, to discuss the influence of the −OH functional group position on the reactivity of the studied unsaturated alcohols.

The atmospheric lifetimes (τ) of these alkenols and the formation of atmospheric degradation products from these compounds are greatly influenced by the presence of the $>C=C<$ double bond (to which OH and NO$_3$ radicals, Cl atoms and O$_3$ molecule can add), and by the presence of different functional groups (Davis and Burkholder, 2011).

Based on these results, the global atmospheric lifetimes and radiative efficiencies (REs) (Pinnock et al., 1995) were calculated for the studied hexenols and the atmospheric implications briefly discussed.

2. Experimental

2.1. Kinetic measurements

The rate coefficients for the reactions (1) and (2) were determined using a conventional relative rate method:

$$OH + alcohol \rightarrow Products \quad (k_i) \quad (3)$$

$$OH + reference \rightarrow Products \quad \left(k_{ref}\right) \quad (4)$$
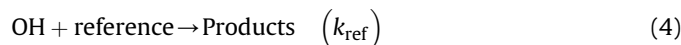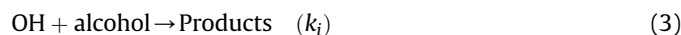
The principle of this method is to measure the decay rate of the alcohol concentration, due to the OH-induced oxidation, relative to a reference compound for which the OH oxidation rate coefficient is well known. Provided that the reactant and the reference compound are lost only by reactions (3) and (4), respectively, it can be shown that:

$$\ln\left(\frac{[\text{alcohol}]_0}{[\text{alcohol}]_t}\right) = \frac{k_i}{k_{ref}}\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \quad (5)$$

where, [alcohol]$_0$, [reference]$_0$, [alcohol]$_t$ and [reference]$_t$ are the concentrations of the alcohol and reference compound at time $t = 0$ and t, respectively, and k_i and k_{ref} are the rate coefficients of the reactions (3) and (4), respectively. Eq. (5) can be compared to a simple linear equation, with a slope equal to k_i/k_{ref} and zero intercept. Provided that k_{ref} is known, the rate coefficient of the reaction (3), k_i, can be determined by multiplying the slope by k_{ref}.

The experimental setup consisted of a greaseless vacuum system, a 200 L collapsible Teflon bag (reaction chamber), and a gas chromatograph (GC-FID, Perkin Elmer Clarus 500) with flame-ionization detection. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of ultra pure N$_2$ or ultra pure air and the bag was then filled to its full capacity at atmospheric pressure. Pressure measurements were performed with a capacitance manometer (MKS Baratron, range 10 Torr).

Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in ultra pure N$_2$ or ultra pure air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h.

The Teflon bag was surrounded by six germicide lamps (Phillips 30 W), providing UV radiation with λ_{max} around 254 nm and six black lamps (Phillips 30 W), providing UV radiation with λ_{max} around 365 nm to produce OH radicals by the UV photolysis of H$_2$O$_2$ or CH$_3$CH$_2$ONO, respectively. When CH$_3$CH$_2$ONO was used as the OH radical source, NO was added to avoid the formation of O$_3$, and, hence, of NO$_3$ radicals (Atkinson et al., 1981). The photolysis time varied from 1.2 to 2.3 min and from 0.8 to 2.3 min for reactions (1) and (2), respectively.

The initial concentrations of the organic compounds (alcohols and references) ranged from 7.3 to 60 ppm (Table 1). When CH$_3$CH$_2$ONO was used as the OH radical source, its initial concentration varied between 35 and 37 ppm and 35 ppm of NO were added. The H$_2$O$_2$ concentrations used were in the range 180–250 ppm, and it was introduced into the chamber with a Hamilton syringe through a stream of ultra pure N$_2$ or ultra pure air. Rate coefficients were measured at (298 $\pm$ 2) K and atmospheric pressure (750 $\pm$ 10) Torr.

Before each set of experiments the Teflon bag was cleaned by filling it with a mixture of O$_2$ and N$_2$ which was irradiated for 20–30 min using the radiation of all of the germicide lamps, to produce O$_3$. After this procedure, the bag was cleaned again by repeated flushing with N$_2$ and checked by gas chromatography that there were no observable impurities, before performing the experiments.

The concentrations of the organic compounds (alcohols and references) were monitored over the course of the reaction by GC-FID. Periodically, gas samples were removed from the Teflon bag using calibrated Hamilton gas syringes (5.0 $\pm$ 0.1) mL and introduced into the gas chromatograph containing an Elite-5 (30 m $\times$ 0.32 mm $\times$ 0.25 mm) capillary column. The chromatographic runs were isothermal and ultra pure He was used as carrier gas.

The rate coefficient k_1 for reaction (1) was measured relative to the rate coefficients of the reaction of OH with allyl ether, 2-methyl-1,3-butadiene and 1-methyl-cyclohexene. The rate coefficient k_2 for reaction (2) was measured relative to the rate coefficients of the reaction of OH with allyl ether, cyclohexene and 1-methyl-cyclohexene.

The mixtures of the alcohols and references with the OH radical source (H$_2$O$_2$ or CH$_3$CH$_2$ONO) were stable in the dark when they were left in the chamber for about 2 h. Moreover, no photolysis of the alcohols or references was observed when mixtures of the reactants, in the absence of the OH radical source, were irradiated for 15 min using the output of all of the germicide lamps (for H$_2$O$_2$) or black lamps (for CH$_3$CH$_2$ONO).

In this work, the method of Pinnock et al. (1995) was used to estimate the radiative efficiencies (REs) directly from the IR spectra of the studied compounds. Spectra were recorded in the 500–1500 cm^{-1} region at 298 K using a Nicolet FTIR spectrometer, with

Table 1
Initial concentration of the reactants, rate coefficient ratios, k_i/k_{ref}, and the relative rate coefficients, k_i, for the reactions of OH radicals with the studied unsaturated alcohols at 298 K and atmospheric pressure.

Alcohol	Runs	[alcohol]$_0$/ppm	Reference	[reference]$_0$/ppm	k_i/k_{ref}	$k_i/10^{-10}$[b]
(Z)-2-hexen-1-ol	1	16.8	Allyl ether	7.3	1.50 ± 0.08	1.0 ± 0.2[c]
	2	8.4		16	1.75 ± 0.04	1.2 ± 0.1[c]
	3	18		18	1.61 ± 0.06	1.1 ± 0.1
	1	20.3	2-Methyl-1,3-butadiene	10	1.10 ± 0.04	1.1 ± 0.3[c]
	2	10		18	1.23 ± 0.04	1.2 ± 0.3[c]
	3	18		18	1.09 ± 0.04	1.1 ± 0.3
	1	15	1-Methylcyclohexene	15	1.06 ± 0.06	1.04 ± 0.08[c]
	2	9		15	1.06 ± 0.06	1.04 ± 0.08
	3[a]	18		9	1.14 ± 0.04	1.07 ± 0.06[c]
			Average			**1.1 ± 0.4**
(E)-3-hexen-1-ol	1	30	Allyl ether	30	1.15 ± 0.06	0.8 ± 0.1[c]
	2	60		30	1.14 ± 0.04	0.8 ± 0.1[c]
	3	30		45	1.14 ± 0.08	0.8 ± 0.1
	1	15	Cyclohexene	30	1.24 ± 0.04	0.79 ± 0.04[c]
	2	45		21	1.23 ± 0.06	0.78 ± 0.05[c]
	3	21		21	1.19 ± 0.04	0.75 ± 0.04
	1	30	1-Methylcyclohexene	30	0.83 ± 0.04	0.81 ± 0.05
	2	60		30	0.86 ± 0.06	0.84 ± 0.05[c]
	3[a]	8		16	0.81 ± 0.02	0.79 ± 0.03[c]
			Average			**0.8 ± 0.1**

[a] Experiments carried out with ethyl nitrite as the OH radicals source.
[b] Units of cm^3 mol^{-1} s^{-1}.
[c] Experiments carried out with ultra pure air as bath gas.

1.0 cm^{-1} resolution. The IR spectra were obtained averaging 4 infrared spectra of the pure compound varying its pressure between 0.2 and 2 Torr. The glass cell was (23.0 ± 0.2) cm long, sealed with NaCl windows. Gas sample pressures were measured with a capacitance manometer (MKS Baratron, range 10 Torr). Background spectra were measured with the sample cell under vacuum. The digitized values of the absorption spectra of the two alcohols are given in the Supplementary material.

2.2. Materials

The chemicals used were N$_2$ (Linde 99.999%. CAS: 7727-37-9), O$_2$ (Linde 99.999%. CAS: 7782-44-7), He (Linde 99.999%. CAS: 7440-59-7), ultra pure air (synthetic air SS Linde), NO (AGA > 99.0%. CAS: 10102-43-9). H$_2$O$_2$ (70,5%. CAS: 7722-84-1) was supplied by Atanor S.A., (Z)-2-hexen-1-ol (95%. CAS: 928-94-9), (E)-3-hexen-1-ol (98%.

CAS: 928-97-2), allyl ether (98%. CAS: 557-40-4), 2-methyl-1,3-butadiene (99%. CAS: 78-79-5), 1-methyl-cyclohexene (97%. CAS: 591-49-1) and cyclohexene (99%. CAS: 110-83-8) were supplied by Sigma Aldrich. Ethyl nitrite was synthesized and purified in our laboratory following Taylor et al. (1980).

The organics were degassed by repeated freeze-pump-thaw cycling and purified by vacuum distillation until gas chromatographic analysis revealed no observable impurities.

Commercially obtained (Z)-2-hexen-1-ol has 95% purity. Of the 5% total impurity, 3% corresponds to the (E)- isomer, and the remaining 2% corresponds to alkanes and alkenes, such as hexane, hexene and 2-butane. Prior to use, it was degassed by freeze-pump-thaw cycling and purified by vacuum distillation. Its purity was checked by GC–MS and NMR before and after purification. After distillation, impurities are almost completely eliminated as revealed by GC–MS and NMR analysis. Hence, we are confident that the IR spectrum of the (Z)-2-hexen-1-ol corresponds to this compound, only.

3. Results and discussion

3.1. Kinetic measurements

The rate coefficients for reactions (1) and (2), measured at (298 ± 2) K and atmospheric pressure, were obtained from the relative loss of the alcohols vs. that of the reference compounds in the presence of OH radicals. The rate coefficients, in units of cm^3 mol^{-1} s^{-1}, of the reaction of OH with the reference compounds used in this work were taken as (6.8 ± 0.7) × 10^{-11} for allyl ether (Peirone et al., 2011), (1.0 ± 0.2) × 10^{-10} for 2-methyl-1,3-butadiene (Atkinson et al., 2006), (9.81 ± 0.18) × 10^{-11} for 1-methylcyclohexene (Aschmann et al., 2012) and (6.35 ± 0.12) × 10^{-11} for cyclohexene (Aschmann et al., 2012) at 298 K.

In order to check the experimental reproducibility, three reference compounds were used for the rate coefficient measurements and, at least, two runs were performed with the same reference compound.

Figs. 1 and 2 show typical plots of ln ([alcohol]$_0$/[alcohol]$_t$) as a function of ln([reference]$_0$/[reference]$_t$). The linearity of the data
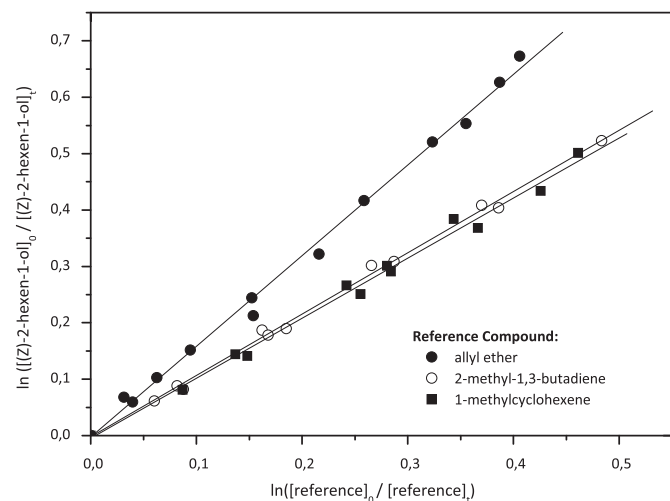

Fig. 1. Typical plots of ln ([(Z)-2-hexen-1-ol]$_0$/[(Z)-2-hexen-1-ol]$_t$) vs. ln ([reference]$_0$/[reference]$_t$) for the reaction of OH with (Z)-2-hexen-1-ol using three different reference compounds at 298 K and 750 Torr.

points, with correlation coefficients >0.99 along with the facts that: i) the plots show practically zero intercepts, ii) no noticeable differences in the obtained rate coefficients were observed using different reference compounds, in the presence or absence of O_2, or with a significant variation of the [alcohol]$_0$/[reference]$_0$ ratios, and iii) the kinetic measurements were carried out at times shorter than one lifetime, suggest that the contribution of secondary reactions with the products of the reactions studied could be considered negligible.

Table 1, shows the alcohols and reference compounds used, their concentrations, the number of runs, the obtained ratios between k_i and k_{ref} and the derived rate coefficients for the reaction of OH radicals with the two studied alcohols.

The main source of error in this method is attributed to the uncertainty associated with k_{ref} which includes systematic errors. The experimental uncertainties are associated with the signal/noise ratio in the measurements of the chromatographic peak areas and the sampling volume uncertainty. For each individual experiment, the experimental errors are quoted as twice the statistical deviation ($2\sigma_{n-1}$) stemming from the least-squares fit of the plots of ln ([alcohol]$_0$/[alcohol]$_t$) vs. ln ([reference]$_0$/[reference]$_t$) which resulted in straight lines with approximately no intercept (<1%). The systematic uncertainties of our determinations are related to, at least, four sources: the sampling volume that is negligible compared with the total volume of the reactor, some hypothetical interference of secondary chemistry which can also be neglected due to the reasons explained above, inadequate integration method of the chromatographic areas and insufficient chromatographic resolution, which was minimized by careful experimental work.

Therefore, we choose to inform values of the rate coefficients that are the average of the independent experiments with the same reference compound. The errors quoted for the average values of k_1 and k_2, encompass the extremes of the individual determinations and the errors of k_1 and k_2 quoted for the individual determinations include the experimental uncertainties and the uncertainties from the reference rate coefficients. We estimate in our measurements an uncertainty of around 10% due to systematic errors that could be added to the final informed value of the rate coefficient.

The recommended rate coefficient values obtained by averaging the values from the different experiments at 298 K, were the following: $k_1 = (1.1 \pm 0.4) \times 10^{-10}$ and $k_2 = (0.8 \pm 0.1) \times 10^{-10}$ (in units of cm^3 mol^{-1} s^{-1}).
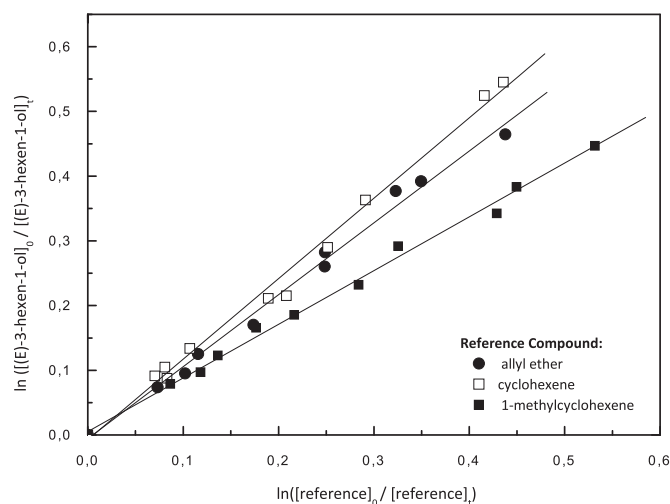

Fig. 2. Typical plots of ln ([(E)-3-hexen-1-ol]$_0$/[(E)-3-hexen-1-ol]$_t$) vs. ln ([reference]$_0$/[reference]$_t$) for the reaction of OH with (E)-3-hexen-1-ol using three different reference compounds at 298 K and 750 Torr.

Table 2
Comparison of the experimental rate coefficients with those calculated using the SAR method, for the reaction of OH radicals with several unsaturated alcohols at 298 K (in units of cm^3 mol^{-1} s^{-1}).

Compound	k_{exp} (OH)/10^{-11}	k_{SAR} (OH)/10^{-11}	k_{SAR}/k_{exp}
CH_2=CHCH$_2$OH	(5.00 ± 0.54)[a]	4.76[h]	1.0
CH_2=CHCH$_2$CH$_2$OH	(5.9 ± 0.9)[b]	5.26	0.9
CH_2=CHCH(OH)CH$_3$	(5.87 ± 0.63)[a]	6.05	1.0
CH_2=CHCH(OH)CH$_2$CH$_3$	(7.12 ± 0.73)[d]	6.57	0.9
CH_2=CHCH(OH)(CH$_3$)CH$_3$	(6.49 ± 0.82)[a]	5.52	0.8
CH_2=CHCH(OH)(CH$_3$)CH$_2$CH$_3$	(6.02 ± 1.80)[f]	6.02[i]	1.0
CH_2=C(CH$_3$)CH$_2$OH	(9.2 ± 1.3)[b]	8.74	0.9
CH_2=C(CH$_3$)CH$_2$ CH$_2$OH	(9.7 ± 1.8)[b]	10.28	1.1
CH_3CH=CHCH$_2$OH	(9.8 ± 1.5)[b]	10.23	1.0
CH_3C(CH$_3$)=CHCH$_2$OH	(15 ± 1)[c]	14.77	1.0
(Z)-CH$_3$CH$_2$CH=CHCH$_2$OH	(10.6 ± 1.5)[e]	9.58	0.9
(Z)-CH$_3$CH$_2$ CH$_2$CH=CHCH$_2$OH	(11 ± 1)[g]	9.58	0.9
(Z)-CH$_3$CH$_2$CH=CHCH$_2$CH$_2$OH	(10.6 ± 1.2)[d]	11.28	1.1
(E)-CH$_3$CH$_2$CH=CHCH$_2$OH	(6.76 ± 0.70)[d]	10.88	1.6
(E)-CH$_3$CH$_2$ CH$_2$CH=CHCH$_2$OH	(6.15 ± 0.75)[d]	10.88	1.8
(E)-CH$_3$CH$_2$CH=CHCH$_2$CH$_2$OH	(8.0 ± 0.1)[g]	12.8	1.6

[a] Takahashi et al. (2010).
[b] Cometto et al. (2008).
[c] Imamura et al. (2004).
[d] Davis and Burkholder (2011).
[e] Orlando and Tyndal (2002).
[f] Bernard et al. (2012).
[g] This work.
[h] The $f_{(R)}$ value of 1.81 for −CH$_2$OH group was used. It was obtained from k_{exp} (CH$_2$=CHCH$_2$OH + OH) (Takahashi et al., 2010), k_{exp} (CH$_2$=C(CH$_3$)CH$_2$CH$_3$ + OH) (Cometto et al., 2008) and k_{exp} (CH$_3$C(CH$_3$) = CHCH$_2$OH + OH) (Imamura et al., 2004).
[i] The $f_{(R)}$ values used were obtained from k_{exp} (CH$_2$=CHCH(OH)(CH$_3$) CH$_2$CH$_3$ + OH) (Bernard et al., 2012).

To the best of our knowledge, there are no other prior reported values of the rate coefficients for reactions (1) and (2). Thus, the present work is the first kinetic study of these reactions and therefore, no direct comparison with the literature can be made.

3.2. Structure−activity relationships (SAR)

A comparison between the experimental rate coefficients (k_{exp}) and the rate coefficients calculated by using the structure−activity relationship (SAR) method (k_{SAR}), developed by Atkinson (1987), for the reaction of unsaturated alcohols with OH radicals is shown in Table 2.

The rate coefficient, k_{SAR}, of alcohols is estimated from the number, position and type of the substituent groups, by multiplying a basic structure rate coefficient, k_{basic}, by one or more group-reactivity factors, $f_{(R)}$, which reflect the type of substituent group attached to the double bond ($f(-CH_3) = 1$, by definition):

$$k_{SAR} = k_{basic} \prod_{i=1}^{i=1-4} f_{(R)} \qquad (6)$$

The k_{basic} values used were those given by Kwok and Atkinson (1995) for OH radical + alkene reactions and the $f_{(R)}$ values obtained by Cometto et al. (2008). The contribution of the H-atom abstraction (from C−H or O−H bonds), to the room-temperature rate coefficients of unsaturated alcohols is generally minor (Grosjean et al., 1993; Aschmann et al., 1997; Orlando et al., 2001), therefore it was not taken into account, assuming that the overall rate of these reactions is determined solely by OH addition to the double bond. The group-reactivity factor for the −CH$_2$OH group (Cometto et al., 2008) was recalculated without considering the (E)-isomers (Table 2).

As can be noted in Table 2, there is very good agreement between the calculated (k_{SAR}) and the experimental rate coefficients

(k_{exp}), the ratio falls in the range $0.8 < k_{SAR}/k_{exp} < 1.1$, except for the ($E$)-isomers of the alcohols for which k_{SAR}/k_{exp}, is in the range 1.6–1.8.

Taking into account that the values of $f_{(R)}$ used in these calculations are all very similar, approximately equal to 2 (Cometto et al., 2008), we can conclude that the reactivity trend of these reactions is mainly determined by the aliphatic structure of the alcohols, corresponding to the k_{basic} values of SAR and, therefore, independent of the location of the double bond with respect to the position of the hydroxyl group, or the −OH bonded to a primary, secondary or tertiary carbon atom.

Differences in k_{exp} between the corresponding (E)- and (Z)-isomers of the unsaturated alcohols are observed in Table 2 and seem to play an important role in determining the compounds' reactivity. At present, we are unable to offer a reasonable explanation to this difference, noting that the relationship k_{SAR}/k_{exp} in Table 2, for the (E)-isomers is close to 2, and that, in this case, the SAR method does not correctly predict the experimentally observed differences in reactivity.

3.3. Atmospheric implications

An important component of the environmental impact of a VOC is its global lifetime, τ_{global}, in the atmosphere, which is the sum of the individual sink processes. It can be obtained considering the following expression:

$$\tau_{global} = \left[\frac{1}{\tau_{Cl}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{other\ processes}}\right]^{-1}$$

(7)

The rate coefficients for the reactions of (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol with NO_3 radicals were measured by Pfang et al. (2006). Unfortunately, there are no data available for the reactions of (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol with O_3 molecules or Cl atoms. Atmospheric photolysis is another potential loss process, but the UV absorption cross-sections (σ) of butenols, pentenols and hexenols have been measured, and it was observed that the absorption vanishes above 290 nm with values of σ smaller than 1×10^{-21} cm^2 mol^{-1} (Jimenez et al., 2009; Aschmann et al., 1997; Cometto et al., 2008; Kirstine et al., 1998; Atkinson et al., 1995; Aschmann et al., 2012). Therefore, it is reasonable to assume that the tropospheric photolysis of the hexenols here studied, is negligible. The term "other processes", takes into account other loss processes in the atmosphere such as dry and wet deposition, heterogeneous reactions, etc. The studied alcohols are expected to be relatively soluble in water (e.g., Henry's law coefficient for different unsaturated alcohols is between 20 and 200 M atm^{-1} at 298 K) (Sander, 1999) so that wet deposition is limited to be of importance. Finally, the volatility of these compounds will render dry deposition an unlikely removal mechanism.

Therefore, an upper limit for the global atmospheric lifetime of the studied unsaturated alcohols was estimated, taking into account the photo-oxidation with OH and NO_3 radicals only (Table 3). The estimated atmospheric lifetimes and global lifetimes of the studied alcohols are presented in Table 3. The lifetimes were calculated using the relationship $\tau_x = 1/k_x$ [X], where [X] is OH or NO_3 radicals. The 12-h average day-time global concentration of OH radicals of 1×10^6 radicals cm^{-3} (global weighted-average concentration) (Prinn et al., 2001), and the 12-h average night-time concentration of NO_3 of 5×10^8 mol cm^{-3} (Atkinson, 2000) were considered for the calculations.

The atmospheric lifetime of both unsaturated alcohols studied is 0.9 h, suggesting that they will be quickly degraded when emitted

Table 3
Experimental rate coefficients for the reactions of studied unsaturated alcohols with OH and NO_3 radicals, the corresponding estimated atmospheric lifetimes and their global lifetimes.

Alcohol	k_{298} (OH)/10^{-11}	k_{298} (NO_3)/10^{-13}	τ_{OH} (h)	τ_{NO_3} (h)	τ_{global} (h)
(E)-3-hexen-1-ol	8.0 ± 1.0[a]	4.43 ± 0.91[b]	3.5	1.2	0.9
(Z)-2-hexen-1-ol	11.0 ± 4.0[a]	3.81 ± 0.38[c]	2.5	1.5	0.9

All of the $k_{(298K)}$ values are in units of cm^3 mol^{-1} s^{-1}. The 12-h average day-time global concentration of OH radicals is 1×10^6 radicals cm^{-3} (global weighted-average concentration) (Prinn et al., 2001). The 12-h average night-time of [NO_3] is 5×10^8 mol cm^{-3} (Atkinson, 2000).
[a] This work.
[b] Pfang et al. (2006).
[c] Zhao et al. (2011).

into the atmosphere and will be involved in tropospheric chemistry on local to regional scales. The estimated global lifetimes are based on the assumption of a uniform distribution of the compounds emitted into the troposphere; however, the calculated lifetimes do not ensure such condition so that the actual lifetime of these compounds will depend on local atmospheric conditions and season.

Calculation of the global warming potential (GWP) for short-lived compounds (with lifetimes shorter than 0.5 years) has not
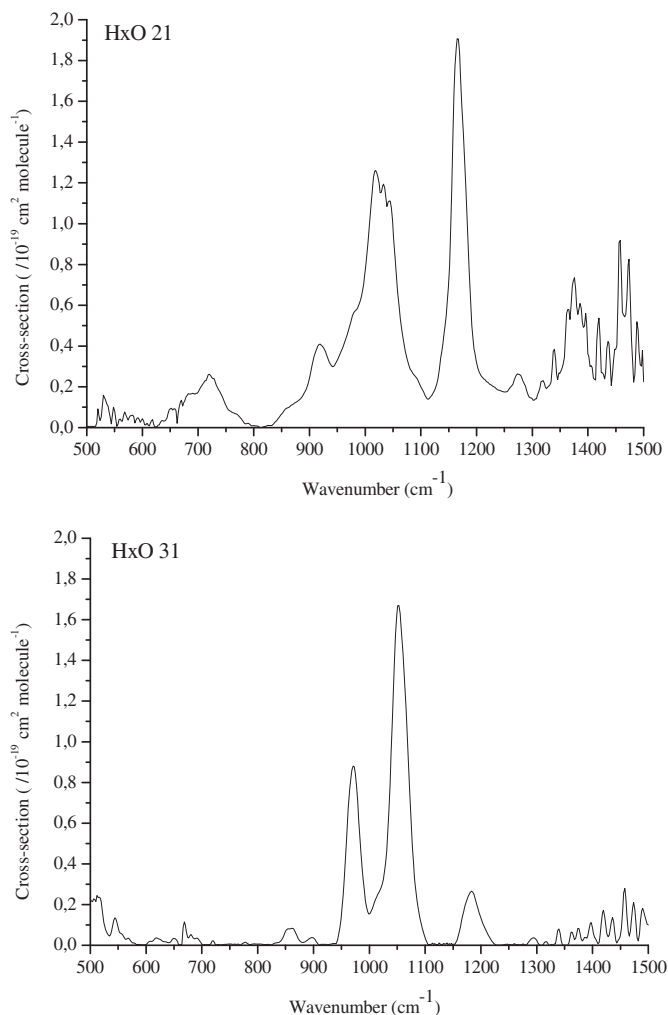

Fig. 3. Plots of cross-section vs. wavenumber of (Z)-2-hexen-1-ol (HxO21) and (E)-3-hexen-1-ol (HxO31).

Table 4
Global lifetimes, estimated RE, GWP and HGWP for the studied unsaturated alcohols.

Alcohol	τ_{global} (years)	RE (W m^{-2})	GWP20	GWP100	HGWP20	HGWP100
(E)-3-hexen-1-ol	1.0×10^{-4}	0.03562	0.0080	0.0012	1.2×10^{-6}	4.9×10^{-7}
(Z)-2-hexen-1-ol	1.0×10^{-4}	0.03826	0.0087	0.0024	1.3×10^{-6}	5.2×10^{-7}
CFCl$_3$	45[a]	0.25[a]	6730[a]	4750[a]	1	1

[a] Forster et al. (2007).

been considered appropriate by the World Meteorological Organization (WMO) (Law and Sturges, 2007), due to the fact that detailed global modeling and emission scenarios would be needed. However, the direct instantaneous cloudy-sky radiative efficiency (RE), which is a necessary parameter to calculate the GWP, involves important spectroscopic information of the studied species in the IR spectral window, where the radiative efficiencies can be significant. In fact, GWPs for short-lived compounds have been reported recently (Nilsson et al., 2009; Baasandorj et al., 2011; Jiménez et al., 2011; Cometto et al., 2011; Aranguren Abrate et al., 2013).

Plots of the cross-sections (cm^2 mol^{-1} cm^{-1}) as a function of wavenumber (cm^{-1}) of the unsaturated alcohols studied are shown in Fig. 3. The integrated IR absorption cross-section (500–1500 cm^{-1}) values for (Z)-HxO21 and (E)-HxO31 are 2.56×10^{-17} and 1.93×10^{-17} (in units of cm^2 mol^{-1} cm^{-1}), respectively. Uncertainties in the cross-section measurements arise from the following sources: the sample concentration (1%), sample purity (3%), path length (1%), spectrum noise and residual baseline offset after subtraction of background (1.5%). Considering these individual uncertainties, we quote a conservative uncertainty of $\pm 6\%$. Unfortunately, there are no literature data for the absorption cross-sections of the studied alcohols to compare with.

The model of Pinnock et al. (1995) for the calculation of RE is also based on the assumption of the uniform distribution of the compound over the troposphere. Radiative efficiencies calculated with this model for short-lived compounds, such as the ones studied in this work, can be significantly lower because their abundances will decrease strongly with altitude. Taking this into account, the calculated REs in the present work should be considered as upper limits.

Table 4 shows the calculated values of the RE for (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol, together with the RE of CFC-11 (Forster et al., 2007) (in units of W m^{-2}) and the calculated values of halocarbon global warming potential (HGWP) and GWP on a time horizon of 20 and 100 years.

The HGWP was calculated relative to CFC-11 using the following expression (Fisher et al., 1990):

$$\text{HGWP} = \frac{\tau_{alcohol}}{\tau_{CFC-11}} \frac{M_{CFC-11}}{M_{alcohol}} \frac{\text{RE}_{alcohol}}{\text{RE}_{CFC-11}} \frac{(1 - \exp^{-t/\tau_{alcohol}})}{(1 - \exp^{-t/\tau_{CFC-11}})} \quad (8)$$

where $\tau_{alcohol}$ and τ_{CFC-11} are the corresponding tropospheric lifetimes, $M_{alcohol}$ and M_{CFC-11} are the corresponding molar masses, $\text{RE}_{alcohol}$ and RE_{CFC-11} are the radiative efficiencies of the alcohols and CFCl$_3$, respectively, and t is the time horizon over which the RE is integrated.

The GWPs of the unsaturated alcohols, relative to CO$_2$, were calculated multiplying the HGWP values by the scaling factors, 6730 and 4750 on a time horizon of 20 and 100 years, respectively (Forster et al., 2007). These scaling factors are the GWP values of the CFC-11.

Summarizing, the lifetime of the studied alcohols indicates that they will be removed from the troposphere in a few hours time. In addition, it is clear from the GWP values that these compounds will not have a significant contribution to the radiative efficiencies of climate change.

Based on studies of the mechanisms for the reactions of the OH radical with unsaturated alcohols (Orlando et al., 2001; Atkinson, 2000; Jimenez et al., 2009; Takahashi et al., 2010), aldehydes and other products with carbonyl groups can be expected for the reactions studied. Identification of the products of these reactions is of great importance because they would be secondary pollutants that are involved in processes such as the photochemical smog (Committee on Aldehydes, 1981) or peroxyacyl nitrates (PANs) formation (Wayne, 2000).

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.11.076.

References

Aranguren Abrate, J.P., Pisso, I., Peirone, S.A., Cometto, P.M., 2013. Relative rate coefficients of OH radical reactions with CF$_3$CF=CClCF$_3$ and CF$_3$CH=CHCH$_2$OH. Ozone depletion potential estimate for CF$_3$CF=CClCF$_3$. Atmos. Environ. 67, 85–92.

Aschmann, S.M., Shu, Y., Arey, J., Atkinson, R., 1997. Products of the gas-phase reactions of cis-3-hexen-1-ol with OH radicals and O$_3$. Atmos. Environ. 31, 3551–3560.

Aschmann, S.M., Arey, J., Atkinson, R., 2012. Kinetics and products of the reactions of OH radicals with cyclohexene, 1-methyl-1-cyclohexene, cis-cyclooctene, and cis-cyclodecene. J. Phys. Chem. A 116, 9507–9515.

Atkinson, R., Carter, W.P.L., Winer, A.M., Pitts Jr., J.N., 1981. An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite photolysis as an OH radical source. J. Air Pollut. Control Assoc. 31, 1090–1092.

Atkinson, R., 1987. A structure–activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. Int. J. Chem. Kinet. 19, 799–828.

Atkinson, R., Arey, J., Aschmann, S.M., Corchnoy, S.B., Shu, Y., 1995. Rate constants for the gas-phase reactions of cis-3-hexen-1-ol, cis-3-hexenylacetate, trans-2-hexenal, and linalool with OH and NO$_3$ radicals and O$_3$ at 296 ± 2 K and OH radical formation yields from the O$_3$ reactions. Int. J. Chem. Kinet. 27, 941–955.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO$_x$. Atmos. Environ. 34, 2063–2101.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J., 2006. Evaluated kinetic and photochemical data for atmospheric chemistry: volume II-gas phase reactions of organic species. Atmos. Chem. Phys. 6, 3625–4055.

Baasandorj, M., Knight, G., Papadimitriou, V.C., Talukdar, R.K., Ravishankara, A.R., Burkholder, J.B., 2011. Rate coefficients for the gas-phase reaction of the hydroxyl radical with CH$_2$=CHF and CH$_2$=CF$_2$. J. Phys. Chem. A 114, 4619–4633.

Bernard, F., Daële, V., Mellouki, A., Sidebottom, H., 2012. Studies of the gas phase reactions of linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol with O$_3$ and OH radicals. J. Phys. Chem. A 116, 6113–6126.

Brahmi, F., Dabbou, S., Flamini, G., Mastouri, M., Issaoui, M., Dhibi, M., Hammami, M., 2012. Chemical composition and biological activities of volatile fractions from three Tunisian cultivars of olive leaves. Med. Chem. Res. 21, 2863–2872.

Cometto, P.M., Dalmasso, P.R., Taccone, R.A., Lane, S.I., Oussar, F., Daele, V., Mellouki, A., Le Bras, G., 2008. Rate coefficients for the reaction of OH with a series of unsaturated alcohols between 263 and 371 K. J. Phys. Chem. A 112, 4444–4450.

Cometto, P.M., Taccone, R.A., Nieto, J.D., Dalmasso, P.R., Lane, S.I., 2011. Kinetic study of the OH radical reactions with CF₃CCl=CCl₂, CF₃CCl=CClCF₃ and CF₃CF=CFCF₃. Atmospheric lifetimes, ozone depletion and global warming potentials. ChemPhysChem 11, 4053–4059.

Committee on Aldehydes, 1981. National Research Council; Formaldehyde and Other Aldehydes. National Academy Press, Washington, DC.

Davis, M.E., Burkholder, J.B., 2011. Rate coefficients for the gas-phase reaction of OH with (Z)-3-hexen-1-ol, 1-penten-3-ol, (E)-2-penten-1-ol, and (E)-2-hexen-1-ol between 243 and 404 K. Atmos. Chem. Phys. 11, 3347–3358.

Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, NY.

Fisher, D.A., Hales, C.H., Wang, W.C., Ko, M.K.W., Sze, N.D., 1990. Model calculations of the relative effects of CFCs and their replacements on global warming. Nature 344, 513–516.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Cambridge University Press, Cambridge, United Kingdom.

Grosjean, D., Grosjean, E., Williams, E.L., 1993. Atmospheric chemistry of unsaturated alcohols. Environ. Sci. Technol. 27, 2478–2485.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global-model of natural volatile organic-compound emissions. J. Geophys. Res. Atmos. 100, 8873–8892.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide and oxides of nitrogen from North America. Atmos. Environ. 34, 2205–2230.

Helming, D., Klinger, L.F., Guenther, A., Vierling, L., Geron, C., Zimmerman, P., 1999. Biogenic volatile organic compound emissions (BVOCs) II. Landscape flux potentials from three continental sites in the U.S. Chemosphere 38, 2189–2204.

Imamura, T., Iida, Y., Obi, K., Nagatani, I., Nakagawa, K., Patroescu-Klotz, I., Hatakeyama, S., 2004. Rate coefficients for the gas-phase reactions of OH radicals with methylbutenols at 298 K. Int. J. Chem. Kinet. 36, 379–385.

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

Jiménez, E., Antiñolo, M., Ballesteros, B., Martínez, E., Albaladejo, J., 2011. Atmospheric lifetimes and global warming potentials of CF₃CH₂CH₂OH and CF₃(CH₂)₂CH₂OH. ChemPhysChem 11, 4079–4087.

Kirstine, W., Galbally, I., Ye, Y., Hooper, M., 1998. Emissions of volatile organic compounds (primarily oxygenated species) from pasture. J. Geophys. Res. 103, 10605–10620.

Kirstine, W.V., Galbally, I.E., 2004. A model for estimating emissions of volatile organic compounds from grass and cut grass in urban airsheds and its application to two Australian cities. J. Air Waste Manag. Assoc. 54, 1299–1311.

Kwok, E.S.C., Atkinson, R., 1995. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure–activity relationship. An update. Atmos. Environ. 29, 1685–1695.

Law, K.S., Sturges, W.T., 2007. Scientific Assessment of Ozone Depletion: 2006. World Meteorological Organization (WMO), Geneva.

Nilsson, E.J.K., Nielsen, O.J., Johnson, M.S., Hurley, M.D., Wallington, T.J., 2009. Atmospheric chemistry of cis-CF₃CH=CHF: kinetics of reactions with OH radicals and O₃ and products of OH radical initiated oxidation. Chem. Phys. Lett. 473, 233–237.

Orlando, J.J., Tyndall, G.S., Ceazan, N., 2001. Rate coefficients and product yields from reaction of OH with 1-penten-3-ol, (Z)-2-penten-1-ol, and allyl alcohol (2-propen-1-ol). J. Phys. Chem. A 105, 3564–3569.

Orlando, J.J., Tyndal, G.S., 2002. Mechanisms for the reactions of OH with two unsaturated aldehydes: crotonaldehyde and acrolein. J. Phys. Chem. A 106, 12252–12259.

Peirone, S.A., Aranguren Abrate, J.P., Taccone, R.A., Cometto, P.M., Lane, S.I., 2011. Kinetic study of the OH-initiated photo-oxidation of four unsaturated (allyl and vinyl) ethers under simulated atmospheric conditions. Atmos. Environ. 45, 5325–5331.

Pfang, C., Martin, R.S., Canosa-Mas, C.E., Wayne, R.P., 2006. Gas-phase reactions of NO₃ and N₂O₅ with (Z)-hex-4-en-1-ol, (Z)-hex-3-en-1-ol (leaf alcohol), (E)-hex-3-en-1-ol, (Z)-hex-2-en-1-ol and (E)-hex-2-en-1-ol. Phys. Chem. Chem. Phys. 8, 354–366.

Pinnock, S., Hurley, M.D., Shine, K.P., Wallington, T.J., Smyth, T.J., 1995. Radiative forcing of climate by hydrochlorocarbons and hydrofluorocarbons. J. Geophys. Res. 100, 23227–23238.

Prinn, R.G., Huang, J., Weiss, R.F., Cunnold, D.M., Fraser, P.J., Simmonds, P.G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R.H.J., Porter, L., Miller, B.R., 2001. Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades. Science 292, 1882–1888.

Reisen, F., Aschmann, S.M., Atkinson, R., Arey, J., 2003. Hydroxyaldehyde products from hydroxyl radical reactions of (Z)-3-hexen-1-ol and 2-methyl-3-buten-2-ol quantified by SPME and API-MS. Environ. Sci. Technol. 37, 4664–4671.

Sander, R., 1999. Max-Planck Institute of Chemistry-Air Chemistry Department. Version 3. <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>.

Takahashi, K., Hurley, M.D., Wallington, T.J., 2010. Kinetics and mechanisms of OH-initiated oxidation of small unsaturated alcohols. Int. J. Chem. Kinet. 42, 151–158.

Taylor, W.D., Allston, T.D., Moscato, M.J., Fazekas, G.B.., Kozlowski, R., Takacs, G.A., 1980. Atmospheric photodissociation lifetimes for nitromethane, methyl nitrite, and methyl nitrate. Int. J. Chem. Kinet. 12, 231–240.

Watkins, P., Wijesundera, C., 2006. Application of zNose™ for the analysis of selected grape aroma compounds. Talanta 70, 595–601.

Wayne, R.P., 2000. Chemistry of Atmospheres. Oxford University Press, New York.

Zhao, Z., Husainy, S., Smith, G.D., 2011. Kinetics studies of the gas phase reactions of NO₃ radicals with series of 1-alkenes, dienes, cycloalkenes, alkenols and alkenals. J. Phys. Chem. A 115, 12161–12172.