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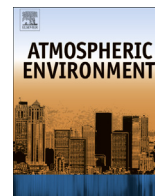


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Rate coefficients at 298 K and 1 atm for the tropospheric degradation of a series of C₆, C₇ and C₈ biogenic unsaturated alcohols initiated by Cl atoms

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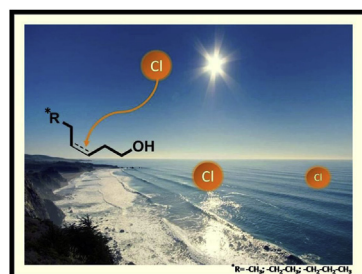
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HIGHLIGHTS

- First kinetic study of Cl + C₆, C₇, C₈ unsaturated alcohols.
- Relative rate coefficients by in situ FTIR detection at 298 K and 1 atm.
- Small increase of the rate coefficient with the chain length.
- Rate coefficients correlated with the HOMO of the unsaturated alcohol.
- Atmospheric lifetimes of hours indicate local impact over on air pollution.

GRAPHICAL ABSTRACT



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(Z)-3-octen-1-ol

Chlorine atoms

ABSTRACT

Rate coefficients for the gas-phase reactions of Cl atoms with a series of unsaturated biogenic alcohols at 298 ± 3 K and 1 atm have been measured by the relative technique in an environmental chamber with in situ FTIR detection of reactants. The rate coefficients obtained using 1-butene and isobutene as reference compounds were (in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_1((E)\text{-2-hexen-1-ol}) = (3.49 \pm 0.82)$, $k_2((E)\text{-3-hexen-1-ol}) = (3.42 \pm 0.79)$, $k_3((Z)\text{-3-hexen-1-ol}) = (2.94 \pm 0.72)$, $k_4((Z)\text{-3-hepten-1-ol}) = (3.80 \pm 0.86)$ and $k_5((Z)\text{-3-octen-1-ol}) = (4.13 \pm 0.68)$. This work constitutes the first kinetic study of the reactions cited above. The rate coefficients are compared with those for other unsaturated alcohols and a correlation between the reactivity of unsaturated alcohols toward Cl atoms and the energy of the HOMO of the unsaturated alcohols is presented. Based on the obtained results, the atmospheric lifetimes of the unsaturated alcohols have been estimated and possible atmospheric implications assessed.

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1. Introduction

The release of oxygenated volatile organic compounds (OVOCs) from plants is well known and unsaturated alcohols such as (Z)-3-hexenol, (E)-2-hexenol and (E)-3-hexenol have been reported to be the compounds predominantly emitted from several plant species (Arey et al. 1991). High fluxes of these unsaturated alcohols have

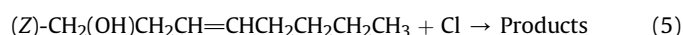
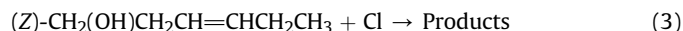
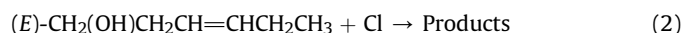
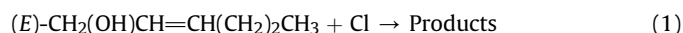
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also been observed after wounding of plants and during drying and pathogen attack (Heiden et al., 2003; Buttery and Ling, 1993; Fall et al., 1999, 2001). Furthermore, recent plague control studies using baited green sticky traps have demonstrated the activity of (Z)-3-hexen-1-ol, in combination with a volatile pheromone, as a potentially effective attractor of the invasive beetle species emerald ash borer (*Agrilus planipennis*) (Ryall et al., 2012). (Z)-3-hepten-1-ol and (Z)-3-octen-1-ol are used extensively as solvents in different industries and are emitted from vegetation, for example, during High-temperature Alfalfa Drying (Dalai et al., 2006). These unsaturated alcohols can also be used as biopesticides for the control of some mosquito species (Cilek et al., 2011).

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 (Guenther et al., 1995). However, this study does not include methanol and the major organic acids emitted from plants, formic acid and acetic acid.

In order to assess possible impacts that these emissions could have on air quality it is necessary to study the reactivity of those compounds toward the major tropospheric oxidants, hydroxyl (OH) and nitrate (NO₃) radicals, ozone (O₃) and chlorine (Cl) atoms, and to understand the degradation pathways and products resulting from the oxidant-mediated degradation. The present study focuses on the determination of rate coefficients for the reactions of Cl atoms with the atmospherically relevant unsaturated alcohols: (E)-2-hexen-1-ol, (E)-3-hexen-1-ol, (Z)-3-hexen-1-ol, (Z)-3-hepten-1-ol and (Z)-3-octen-1-ol :



Although for unsaturated VOCs reactions with OH, and to a lesser extent NO₃ and O₃ are generally deemed the most important removal processes reaction with chlorine atoms can play an important role in atmospheric chemistry since atomic Cl generally reacts with organic compounds an order of magnitude faster than OH. Chlorine atoms have generally been thought to be produced primarily from the photolysis of molecular chlorine originating from heterogeneous reaction cycles involving sea salt (Erickson et al., 1999; Keene et al., 1999; Knipping and Dabdub, 2003). In coastal urban areas for a brief period at dawn it is estimated that the concentration of Cl atoms produced from the photolysis of molecular chlorine (Cl₂) can be 1×10^5 atoms cm⁻³ or higher in the marine boundary layer (Spicer et al., 1998; Ezell et al., 2002; Lawler et al., 2009). At this Cl atom level reactions with chlorine atoms in coastal areas can make a significant contribution to the degradation of VOCs. Furthermore, the detection of significant levels of photolabile nitryl chloride (ClNO₂) species in mid-continental areas has expanded the potential impact of Cl to tropospheric oxidation chemistry (Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011). Riedel et al., 2012 have recently shown that both ClNO₂ and HCl are significant Cl atom sources in the Los Angeles basin with Cl-atom mediated reactions accounting for ~25% of the alkane degradation which implies also substantial contributions for other fast reacting VOCs.

While there are now many studies on the reactions of Cl atoms with a variety OVOCs available in the literature (Calvert et al., 2011)

there are only a few for unsaturated alcohols in comparison to the many kinetic and product studies for the reactions of saturated alcohols with OH radicals and O₃ (Atkinson and Arey, 2003; Mellouki et al., 2003; Calvert et al., 2011; Bernard et al., 2012). Using a relative kinetic technique Rodríguez et al. (2007) reported rate coefficients for the reactions of Cl atoms with 3-buten-2-ol and 2-methyl-3-buten-2-ol over the temperature range 256–298 K and for 2-propen-1-ol at room temperature. Again using the relative kinetic technique. Rodríguez et al. (2008, 2009) measured rate coefficients for the reactions of Cl atoms with 2-buten-1-ol, 2-methyl-2-propen-1-ol and 3-methyl-2-buten-1-ol as a function of temperature over the range 255–298 K. Liang et al. (2011) have reported rate coefficients for the reactions of Cl atoms with 3-buten-1-ol and 2-buten-1-ol measured over the temperature range 298–363 K using a relative kinetic technique. Fantechi et al. (1998) and Ferronato et al. (1998) have both measured the rate coefficient for the reaction of Cl with 2-methyl-3-buten-2-ol using relative kinetic methods but Rodríguez et al. (2007) have argued that the values obtained may be too high due to experimental artifacts. Finally, Rodríguez et al. (2010) have determined the rate coefficients for two pentenols, 1-penten-3-ol and (Z)-2-penten-1-ol, over the temperature range 258–333 K using a relative kinetic method and have also reported that the reactions result, under their experimental NOx-free conditions, in the formation of large yields of halogenated and non-halogenated aldehydes.

The oxidation of unsaturated alcohols with the major atmospheric oxidants has been shown to produce secondary pollutants such as ozone and oxygenates, impacting both the chemical composition of the troposphere and its oxidizing capacity (Shu et al., 1997; Atkinson and Arey, 2003). Furthermore, high yields of secondary organic aerosol (SOA) have been observed in the OH radical and ozone induced degradation of unsaturated alcohols (Bernard et al., 2012), the same effect is expected for Cl atoms reactions.

Rate coefficients determined for reactions (1)–(5) at atmospheric pressure and room temperature using a relative kinetic technique are presented and a comparison is made with the reactivity of other unsaturated alcohols and the parent alkenes toward Cl atoms. In addition, to estimates of tropospheric lifetimes for the five alcohols studied with respect to reaction with the major atmospheric oxidants, a correlation between the Cl rate coefficients of the unsaturated alcohols and the energy of the highest occupied molecular orbital (E_{HOMO}) of the alkene entity in the compounds is presented.

2. Experimental

All the experiments were performed in a 480 L chamber at 298 ± 3 K in 1 atm of synthetic air. A detailed description of the reactor can be found elsewhere and only a brief general description is given here (Barnes et al., 1993).

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 magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. The reactor contains 24 fluorescent lamps (Philips TLA 40 W, $300 \leq \lambda \leq 450$ nm, $\lambda_{\text{max}} = 360$ nm) spaced evenly around the outside of the reactor. It can be evacuated by a pumping system consisting of a turbomolecular pump backed by a double stage rotary pump to 10^{-3} Torr.

A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer Nicolet Magna 520 equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector enables in situ monitoring of the reactants in the infrared

range 4000–700 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.

Chlorine atoms were generated by the photolysis of Cl_2 in air with the fluorescent lamps:



The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were: (*E*)-2-hexen-1-ol (3–4), (*E*)-3-hexen-1-ol (3–4), (*Z*)-3-hexen-1-ol (3–4), (*Z*)-3-hepten-1-ol (2–3) and (*Z*)-3-octen-1-ol (2–3), isobutene (4–5), 1-butene (4–5) and Cl_2 (8–9).

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): (*E*)-2-hexen-1-ol at 1388.7 and 3653.7, (*E*)-3-hexen-1-ol at 1050.8, 1385.8 and 3619.3, (*Z*)-3-hexen-1-ol at 1053.6 and 3616.5, (*Z*)-3-hepten-1-ol 1053.7 and 3616.5, (*Z*)-3-octen-1-ol 1054.1 and 3616.8, isobutene at 889.2 and 1-butene at 910.8.

Rate coefficients for the reactions of Cl atoms with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol were determined by comparing their rate of decay with that of the corresponding decay of the two reference compounds 1-butene and isobutene:



Provided that the reference compound and the alcohol are lost only by reactions (7) and (8), then it can be shown that:

$$\ln \left\{ \frac{[\text{Alcohol}]_0}{[\text{Alcohol}]_t} \right\} = \frac{k_7}{k_8} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (I)$$

where, $[\text{Alcohol}]_0$, $[\text{Reference}]_0$, $[\text{Alcohol}]_t$ and $[\text{Reference}]_t$ are the concentrations of the alcohol and the reference compound at times $t = 0$ and t , respectively, and k_7 and k_8 are the rate coefficients of reactions (7) and (8), respectively.

The relative rate technique relies on the assumption that the alcohol and the reference compounds are removed solely by reaction with Cl atoms. To verify this assumption, mixtures of Cl_2 in air with the alcohol of interest and the reference compound were prepared and allowed to stand in the dark for two hours. In all cases, the reaction of the organic species with the precursor of Cl atoms, in the absence of UV light, was of negligible importance, however, these tests revealed significant wall loss for (*Z*)-3-octen-1-ol ($\text{C}_3\text{O}_1\text{O}_1$). Furthermore, to test for possible photolysis of the reactants mixtures of the alcohols in air, in the absence of Cl, were irradiated for 30 min using the output of all the lamps surrounding the chamber. No significant photolysis of any of the reactants was observed and the wall loss of (*Z*)-3-octen-1-ol ($\text{C}_3\text{O}_1\text{O}_1$) was also not affected. To account for the wall loss of (*Z*)-3-octen-1-ol ($\text{C}_3\text{O}_1\text{O}_1$) in the kinetic analysis the following modified version of Eq. (I) was used:

$$\ln \left\{ \frac{[\text{C}_3\text{O}_1\text{O}_1]_0}{[\text{C}_3\text{O}_1\text{O}_1]_t} \right\} - k_{\text{wall}}(t - t_0) = \frac{k_7}{k_8} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (II)$$

where k_{wall} is the first order wall loss rate coefficient for (*Z*)-3-octen-1-ol. The wall loss for (*Z*)-3-octen-1-ol was determined in

each experiment during a dark period prior to switching on the photolysis lamps.

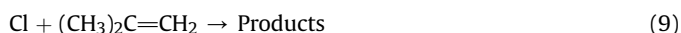
3. Materials

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%), isobutene (Messer Griesheim, 99%), 1-butene (Messer Griesheim, 99%), Cl_2 (Messer Griesheim, >99.8%). (*E*)-2-hexen-1-ol (Alfa Aesar, 97%), (*E*)-3-hexen-1-ol (Alfa Aesar, 97%) and (*Z*)-3-hexen-1-ol (Alfa Aesar, 98%), (*Z*)-3-hepten-1-ol (Alfa Aesar, 97%), (*Z*)-3-Octen-1-ol (Alfa Aesar, 95%).

4. Results and discussion

Fig. 1 shows the kinetic data obtained from the investigation for the reaction of Cl with (*Z*)-3-hexen-1-ol (as an example of hexenol isomer), (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol relative to two different reference compounds. For clarity, in Fig. 1 only one example for the unsaturated alcohol and reference compound combination is shown. At least two experiments have been performed for each reference compound and reasonable linear relationships were obtained in all cases. The linearity of the plots with zero or near-zero intercepts, combined with the fact that similar results were obtained with two different reference organics, supports that complications due to secondary reactions in the experimental systems were negligible.

Table 1 lists the rate coefficient ratios $k_{\text{Alcohol}}/k_{\text{Reference}}$ obtained in the individual experiments at 298 K for each unsaturated alcohol and reference compound combination. The wall deposition correction in the case of (*Z*)-3-octen-1-ol was between 20 and 25%. The errors for the ratios $k_{\text{Alcohol}}/k_{\text{Reference}}$ are the 2σ statistical errors from the linear regression fits to the plots. The absolute values of the rate coefficients k_{Alcohol} listed in Table 1 for reactions (1–5) measured relative to reactions (9) and (10):



were put on an absolute footing using $k_9 = (3.40 \pm 0.28) \times 10^{-10}$ and $k_{10} = (3.38 \pm 0.48) \times 10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$ for the reaction of Cl with isobutene and 1-butene, respectively (Ezell et al., 2002). The errors quoted for the individual k_{Alcohol} values are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have added the error associated with the reference rate coefficients for reactions (9) and (10).

As can be seen in Table 1 there is good agreement not only between the individual rate coefficients obtained with each reference compound but also between the values of the rate coefficients obtained with both reference compounds. We, therefore, prefer to quote final rate coefficients for the reactions of Cl with each unsaturated alcohol which are an average of all the individual values determined for that compound. The following averaged rate coefficients have been thus obtained for the reaction of Cl with the unsaturated alcohols at 298 ± 2 K and atmospheric pressure:

$$\begin{aligned} k_1 &= (3.49 \pm 0.82) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ k_2 &= (3.42 \pm 0.79) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ k_3 &= (2.94 \pm 0.72) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ k_4 &= (3.80 \pm 0.86) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ k_5 &= (4.13 \pm 0.68) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \end{aligned}$$

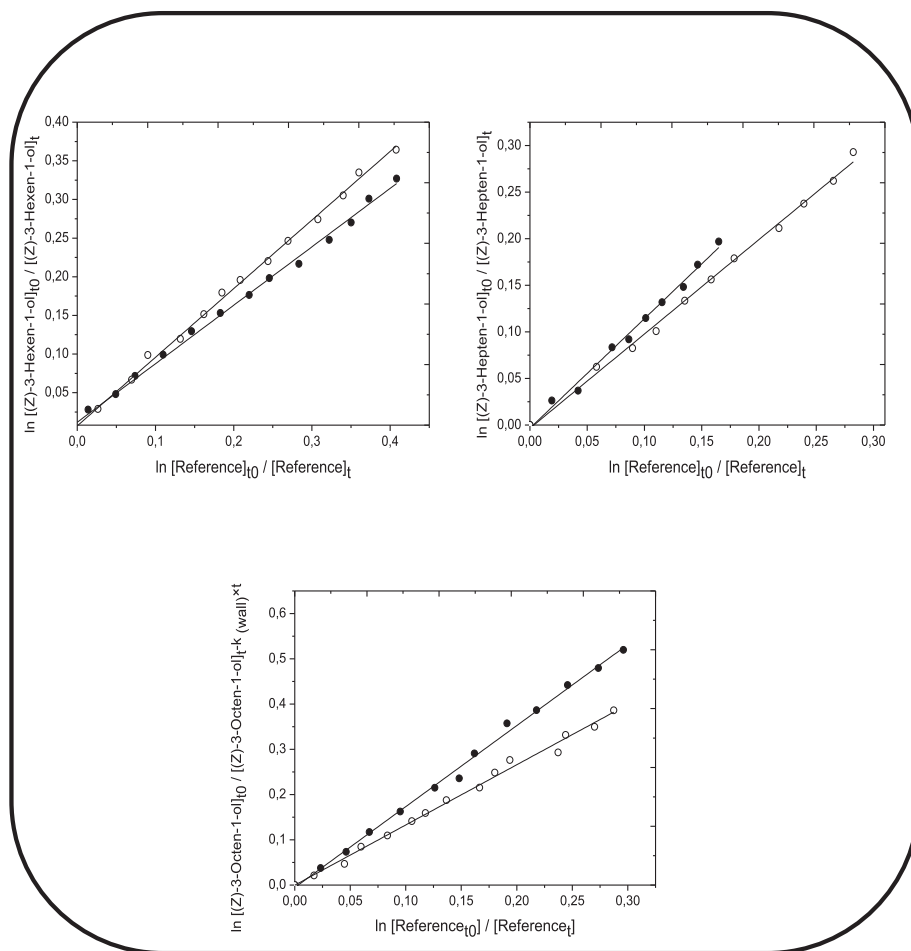


Fig. 1. Plot of the kinetic data for the reaction of (Z)-3-hexen-1-ol, (Z)-3-hepten-1-ol and (Z)-3-octen-1-ol with Cl atoms using isobutene (●) and 1-butene (○) as reference hydrocarbons.

The final errors given for the averaged rate coefficients given above and listed in Table 1 are the square root of the sum of the squares of the individual errors for each kinetic determination.

4.1. Reactivity trends

There are no other measurements available in the literature with which the rate coefficients measured in this study for the five unsaturated alcohols can be compared. There is very little difference between the rate coefficients for the unsaturated alcohols. This is not surprising since the rate coefficients are at or near the gas kinetic limit and the precision of the measurements is not high enough to be able to discern subtle differences in the reactivities toward Cl. In spite of this, for the straight chained unsaturated alcohols studied in this work, although not larger than the errors limits, there is a small but perceptible increase in the rate coefficients on increasing the length of the carbon change, i.e. $k_{\text{hexenol}} < k_{\text{heptenol}} < k_{\text{octenol}}$.

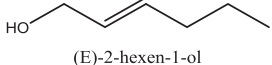
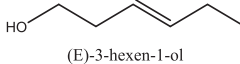
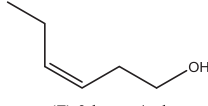
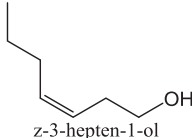
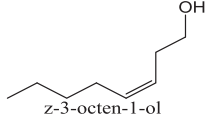
For linear alkanols, C₁–C₈, an analysis of the rate data for reaction with Cl shows that there is a near regular increase in the rate coefficient for each inserted –CH₂– moiety with a mean incremental increase of $\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Nelson et al., 1990; Cheema et al., 2002). A similar trend is also observable for the reactions of Cl with terminal alkenes although the observed increase is not so regular (Ezell et al., 2002; Walavalkar et al., 2013). Table 2 lists the rate coefficients at 298 K obtained in this work for

reactions (1–5) and for the reactions of Cl with other C₃–C₅ unsaturated alcohols.

In Table 2, the rate coefficients for alkenols above C₅ are near the collision-controlled regime and trends are not easily discernible. In addition, a series of measurements unfortunately does not exist for C₃–C₈ alkenols where the distance between the OH-containing carbon and the double bond is sequentially increased by the insertion of a –CH₂– group. However, for the C₃–C₅ alkenols, where the rate coefficients are still below the gas kinetic limit, some reactivity trends are discernible. For the unsaturated alcohols in Table 2 with a terminal OH group there is clear increase in the reactivity, which is larger than the error limits of the measurements, on going from C₃ to C₅. Alkylation of the double bond has the expected effect of increasing the reactivity of the compound toward electrophilic addition of Cl atoms as can be seen when comparing the rate coefficients for 2-propen-1-ol, 2-buten-1-ol, 3-methyl-2-buten-1-ol and 2-penten-1-ol.

The presence of the OH group on the carbon in the α -position to the double bond would appear to have a deactivating effect as illustrated by the low Cl rate coefficients reported for 2-propen-1-ol, 3-buten-2-ol, 2-methyl-2-propen-1-ol, and 1-penten-3-ol. 2-Methyl-3-buten-2-ol would also fit this trend if the lowest of the reported values for its reaction with Cl is the most accurate value. The apparent deactivating effect in the OH in an α -position is seen quite clearly when comparing the rate coefficients for the reactions of Cl with 3-buten-2-ol and 3-buten-1-ol where shifting the OH

Table 1
Rate coefficient ratios $k_{\text{Alcohol}}/k_{\text{Reference}}$ and rate coefficients for the reactions of Cl atoms with (*E*)-2-hexen-1-ol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol at (298 ± 3) K in 1 atm of air.

| Unsaturated alcohol | Reference | $k_{\text{Alcohol}}/k_{\text{Reference}}$ | $k_{\text{Alcohol}} \times 10^{10} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ |
|--|--|---|---|
|  (<i>E</i>)-2-hexen-1-ol | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ Average | (0.89 ± 0.02) (1.09 ± 0.02) (1.07 ± 0.02) (1.06 ± 0.03) (3.49 \pm 0.82) | (3.03 ± 0.25) (3.71 ± 0.31) (3.62 ± 0.51) (3.59 ± 0.51) (3.49 \pm 0.82) |
|  (<i>E</i>)-3-hexen-1-ol | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ Average | (0.96 ± 0.02) (1.05 ± 0.06) (1.09 ± 0.04) (0.95 ± 0.03) (3.42 \pm 0.79) | (3.27 ± 0.27) (3.57 ± 0.29) (3.67 ± 0.52) (3.20 ± 0.45) (3.42 \pm 0.79) |
|  (<i>Z</i>)-3-hexen-1-ol | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ Average | (0.82 ± 0.02) (0.76 ± 0.01) (0.89 ± 0.01) (1.00 ± 0.03) (2.94 \pm 0.72) | (2.80 ± 0.23) (2.57 ± 0.21) (3.00 ± 0.43) (3.37 ± 0.48) (2.94 \pm 0.72) |
|  z-3-hepten-1-ol | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ Average | (1.17 ± 0.06) (1.18 ± 0.04) (1.07 ± 0.03) (1.06 ± 0.05) (3.80 \pm 0.86) | (3.98 ± 0.33) (4.00 ± 0.33) (3.62 ± 0.51) (3.60 ± 0.51) (3.80 \pm 0.86) |
|  z-3-octen-1-ol | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ Average | (1.67 ± 0.04) (1.79 ± 0.03) (1.47 ± 0.04) (1.58 ± 0.64) (4.13 \pm 0.68) | (4.27 ± 0.35) (4.66 ± 0.38) (3.97 ± 0.33) (3.63 ± 0.29) (4.13 \pm 0.68) |

group further away to a carbon β to the double bond results in an increase of the rate coefficient by a factor of 1.8.

The rate coefficients for the reactions of Cl with propene, 1-butene and 1-pentene (in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are 2.64, 3.38 and 3.97 (Ezell et al., 2002), respectively, which are significantly higher than the values of 1.72, 1.44 and 2.35 reported for the reactions of Cl with 2-propen-1-ol, 3-buten-2-ol and 1-penten-3-ol (Table 2). This series would again appear to highlight a deactivating effect of the OH group which positioned α to the double bond. This apparent deactivating effect toward Cl addition to the double bond is completely opposite to what has been observed for the reactions of OH radicals with alkenols where activation of the double bond toward OH addition was observed for the substituent groups $\text{C}(\text{OH})(\text{CH}_3)_2$, CH_2OH and $\text{CH}(\text{OH})\text{CH}_3$ (Papagni et al., 2001). It should be borne in mind when making these reactivity comparisons that absolute and relative measurements of Cl rate coefficients with VOCs (Liang et al., 2011; Xing et al., 2009) and the majority of the rate coefficients listed in Table 2 for the reactions of Cl with alkenols have been determined only once. Furthermore, quite a few of them were reported only by one research group and where more than one determination is available, as for 2-methyl-3-buten-2-ol, there is a large discrepancy in the reported values. To validate the deactivating effect of the OH group located on the α -carbon to the double bond further measurements by several other groups are obviously necessary.

Aschmann and Atkinson (1995) have developed a structure activity relationship (SAR) for the reaction of Cl atoms with alkanes which proceed by simple hydrogen abstraction. Using the Aschmann and Atkinson Cl-SAR for alkanes as a basis (Ezell et al., 2002), in a structure and reactivity analysis of the reaction of Cl with

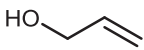
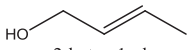
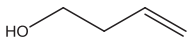
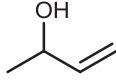
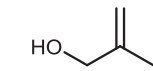
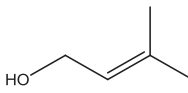
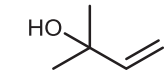
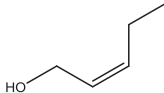
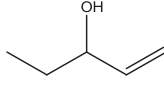
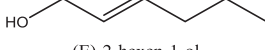
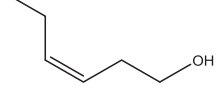
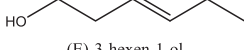
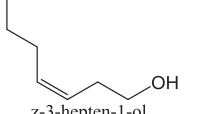
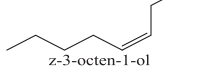
alkenes, have obtained rate coefficients for addition of Cl to the double bond in the alkenes and also rate coefficients for the abstraction of the allylic hydrogen atoms, i.e. the hydrogen atoms on the carbon atoms directly attached to the double bond. The rate coefficients estimated using the Cl-SAR for a series of branched- and straight-chained alkenes developed by Ezell et al. (2002) agreed extremely well with the literature values. Interestingly the rate coefficients determined by Ezell et al. (2002) for addition of Cl to the double bonds of propene, 1-butene and 1-pentene are significantly higher than the overall rate coefficients for the reactions of Cl atoms with the corresponding unsaturated alcohols.

Cheema et al. (2002) in their study on the reaction of Cl with propanol have derived a rate coefficient of $8.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for H-atom abstraction from the $-\text{CH}_2\text{OH}$ group. This value is likely to be considerably lower when the $-\text{CH}_2\text{OH}$ is directly attached to a double bond. Cheema et al. (2002) also found evidence that the OH group lowers the rate coefficient for attack at the β - CH_2 in linear alcohols. All the above factors and the present limited kinetic data set for alkenols with high associated uncertainty in the rate coefficients makes it difficult to use the data to further develop the Cl-SAR of Ezell et al. (2002) so that it can be applied to alkenols.

For the $>\text{C}_5$ alkenols in Table 2 the rate coefficients for reaction with Cl are generally just slightly lower or similar those for the analogous alkene + Cl reactions we could find in the literature (Ezell et al., 2002; Walavalkar et al., 2013). This probably just reflects that the rate coefficients are already in the collision-limited regime where changes in the molecular topography of the alkenols play no further perceptible role at the present available precision of the experimental methods.

Table 2

Rate coefficients for the reactions of chlorine atoms with unsaturated alcohols at 298 K and atmospheric pressure.

| Unsaturated alcohol | $k_{\text{Cl}} \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1}$ | Reference |
|---|---|--|
|  | 1.72 ± 0.19 | Rodríguez et al. (2007) |
| 2-propen-1-ol | | |
|  | 3.12 ± 0.64 | Rodríguez et al. (2008, 2009) |
| 2-buten-1-ol | 3.90 ± 0.35 | Liang et al. (2011) |
|  | 2.63 ± 0.25 | Liang et al. (2011) |
| 3-buten-1-ol | | |
|  | 1.44 ± 0.17 | Rodríguez et al. (2007) |
| 3-buten-2-ol | | |
|  | 2.17 ± 0.39 | Rodríguez et al. (2008, 2009) |
| 2-methyl-2-propen-1-ol | | |
|  | 4.02 ± 0.56 | Rodríguez et al. (2008, 2009) |
| 3-methyl-2-buten-1-ol | | |
|  | 4.8 ± 1.0^a 3.3 ± 0.4^a 2.13 ± 0.19 | Fantechi et al. (1998) Ferronato et al. (1998) Rodríguez et al. (2007) |
| 2-methyl-3-buten-2-ol | | |
|  | 3.00 ± 0.49 | Rodríguez et al. (2010) |
| (Z)-2-penten-1-ol | | |
|  | 2.35 ± 0.31 | Rodríguez et al. (2010) |
| 1-penten-3-ol | | |
|  | 3.49 ± 0.82 | This work |
| (E)-2-hexen-1-ol | | |
|  | 2.94 ± 0.72 | This work |
| (Z)-3-hexen-1-ol | | |
|  | 3.92 ± 0.79 | This work |
| (E)-3-hexen-1-ol | | |
|  | 3.80 ± 0.86 | This work |
| z-3-hepten-1-ol | | |
|  | 4.13 ± 0.68 | This work |
| z-3-octen-1-ol | | |

^a Rate coefficients possibly too high because of experimental artefacts (Rodríguez et al., 2007).

4.2. Free energy relationships

The ionization potential (IP) or the energy of the highest occupied molecular orbital (HOMO) of unsaturated VOCs can be correlated with the reactivity of different kinds of electrophiles such as O and Cl atoms, OH and NO₃ radicals and O₃ molecules toward alkenes, methyl-substituted alkenes and more recently to unsaturated OVOCs (Atkinson, 1997; Wayne et al., 1991; Baumgartner et al., 2002; Blanco et al., 2009a,b,c; Grosjean and Williams, 1992). The correlation between the E_{HOMO} of the unsaturated VOCs and the rate coefficients can be represented in the following simplified form for a limited range of E_{HOMO} values:

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

The E_{HOMO} and the rate coefficients obtained in this work and the rate coefficients for the reactions of other OVOCs with Cl atoms obtained in previous studies are listed in Table 3. The HOMO energies for the unsaturated compounds listed in Table 3 were calculated 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 then calculated by Moller-Plesset perturbation theory (MP4-SCF) using an “ab initio” Hamiltonian with a 6–311++ G(d,p) basis set. The correlation obtained in our previous study for a number of different compounds (esters, ketones, aldehydes, alcohols, and alkenes) was (Blanco et al., 2009a):

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

The Cl rate coefficients obtained in this work have incorporated into our previous reported correlation between k_{Cl} and E_{HOMO} for a series of unsaturated organic compounds to update the equation. The updated relationship resulting from incorporation of the new data is as follows (Fig. 2):

$$\ln k_{\text{Cl}} \left(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \right) = -(0.3 \pm 0.1) E_{\text{HOMO}} - (19.0 \pm 1.4) \quad (\text{IV})$$

The quality of the correlation is such that estimations can be made of rate coefficients for reactions which have not yet been experimentally investigated.

4.3. Atmospheric implications

The rate coefficients obtained in this study for the reactions of Cl atoms with the C₆–C₈ alkenols can be used in combination with rate coefficients for their reactions with other oxidants to estimate their tropospheric lifetimes with respect to each oxidant. The atmospheric lifetime, τ_x , can be calculate using the expression: $\tau_x = 1/k_x[X]$ where [X] is the typical atmospheric concentration of the oxidant (X = OH, Cl, NO₃ or O₃) and k_x is the rate coefficient for the reaction of the oxidant X.

The estimated tropospheric lifetimes at room temperature of the unsaturated alcohols with the tropospheric oxidants OH, Cl, NO₃ and O₃, are listed in Table 4 and were calculated using the rate coefficients obtained in this work for chlorine atoms, and from the literature for the other oxidants.

For (Z)-3-hepten-1-ol and (Z)-3-octen-1-ol there are no rate coefficients for their reactions with OH, NO₃ and O₃ available in the literature, and similarly for the reactions of (E)-2-hexen-1-ol and (E)-3-hexen-1-ol with O₃. However, the rate coefficients for the reactions of the oxidants with these alkenols and, thus the

Table 3
Rate coefficients of the reactions of Cl atoms with different unsaturated VOCs and HOMO energies for the corresponding VOCs calculated using the Gaussian 03 package.

| VOC | E _{HOMO} (eV) | k _{Cl} (cm ³ molecule ⁻¹ s ⁻¹) | ln k _{Cl} |
|--|------------------------|---|--------------------|
| 1- CH ₂ =CHCN | 10.89 ^a | 1.11E-10 | -22.92149091 |
| 2- CH ₂ =CHCH ₃ | 10.11 ^b | 2.45E-10 | -22.12976291 |
| 3- CH ₂ =CHOCH ₂ CH ₃ | 9.57 ^b | 3.30E-10 | -21.83192846 |
| 4- CH ₂ =CHCH ₂ OH | 10.36 ^c | 1.72E-10 | -22.48352664 |
| 5- CH ₂ =CHC(O)H | 10.69 ^b | 2.10E-10 | -22.28391359 |
| 6- CH ₂ =CHC(O)CH ₃ | 10.72 ^b | 2.20E-10 | -22.23739357 |
| 7- CH ₂ =CHC(O)OH | 11.14 ^a | 3.99E-10 | -21.6420597 |
| 8- CH ₂ =CHC(O)OCH ₃ | 11.06 ^d | 2.04E-10 | -22.31290112 |
| 9- CH ₂ =CHC(O)O(CH ₂) ₃ CH ₃ | 11.04 ^e | 2.50E-10 | -22.1095602 |
| 10- CH ₂ =C(CH ₃)C(O)OCH ₃ | 10.56 ^d | 2.82E-10 | -21.98911404 |
| 11- CH ₂ =C(CH ₃)C(O)O(CH ₂) ₃ CH ₃ | 10.53 ^d | 3.60E-10 | -21.74491708 |
| 12- CH ₂ =CHCH ₂ OC(O)CH ₃ | 10.41 ^e | 1.30E-10 | -22.76348667 |
| 13- CH ₂ =CHOC(O)CH ₃ | 10.64 ^f | 2.68E-10 | -22.04003414 |
| 14- (E)-2-HOCH ₂ CH ₂ CH=CHCH ₂ CH ₃ | 9.44 ^g | 3.49E-10 | -21.77594919 |
| 15- (E)-3-HOCH ₂ CH=CH(CH ₂) ₂ CH ₃ | 9.58 ^g | 3.42E-10 | -21.79621038 |
| 16- CH ₂ =CHCH ₂ CH ₂ CH ₂ OH | 10.18 ^h | 2.35E-10 | -22.1714356 |
| 17- HOCH ₂ CH ₂ CH=CHCH ₂ CH ₂ CH ₃ | 9.50 ^g | 3.80E-10 | -21.71751811 |
| 18- HOCH ₂ CH ₂ CH=CHCH ₂ CH ₂ CH ₂ CH ₃ | 9.46 ^g | 4.13E-10 | -21.60757352 |

^a Teruel et al. (2007).

^b NIST – Chemical Kinetics Data Base on the Web.

^c Rodríguez et al. (2007).

^d Blanco et al. (2009a,c).

^e Blanco et al. (2009a,c).

^f Blanco et al. (2009a,b,c).

^g This work.

^h Rodríguez et al. (2010).

respective atmospheric lifetimes, are not expected to be significantly different to those of the other alkenols in the table for which kinetic data is available. The following typical atmospheric concentrations were used in the estimations of τ_X : a 12 h daylight average OH concentration of $[OH] = 2 \times 10^6$ molecule cm⁻³ (Hein et al., 1997), a 12 h night-time average NO₃ concentration of $[NO_3] = 5 \times 10^8$ molecule cm⁻³ (Atkinson, 2000), a 24 h average O₃ concentration of 7×10^{11} molecule cm⁻³ (Logan, 1985), and an average of chlorine atoms concentration of $[Cl] = 1 \times 10^4$ molecule cm⁻³ (Wingenter et al., 1996).

As seen from Table 4 the OH-radical initiated oxidation during daylight hours and the NO₃-radical initiated degradation during night-time the dominant homogeneous loss process of the C₆–C₈ alkenols in troposphere. In polluted areas, where peak concentrations of O₃ molecules as high as 5×10^{12} molecules cm⁻³ can occur, the available literature kinetic data suggests that O₃-molecule

initiated degradation of hexenols can also compete as an atmospheric sink of these unsaturated alcohols. At the Cl atom concentration used in the lifetime calculations the contribution of Cl to the degradation of the C₆–C₈ alkenols will be of negligible importance. Reaction with chlorine atoms will only be of atmospheric significant for the degradation of the C₆–C₈ alkenols in polluted urban areas and marine coastal regions where the Cl-atom concentration can reach levels of 1×10^5 molecule cm⁻³ or higher (Singh et al., 1996; Riedel et al., 2013 and references therein). However, the lifetimes given in Table 4 are crude estimates and the true loss rates are expected to vary greatly depending on local atmospheric conditions.

From the few product studies which have been performed on the OH, ozone, NO₃ induced atmospheric degradation of unsaturated alcohols it is known that the major products consist of a variety of aldehydes, ketones and organic nitrates (Bernard et al., 2012; Calvert et al., 2011; Noda et al., 2000; Noda and Ljungstrom, 2002). Cl-atom induced degradation will result in the formation of halogenated aldehydes and ketones. Further reactions of the aldehydes and ketones in NO_x rich environments will lead to

Table 4

Estimated atmospheric lifetimes for the reactions of the C₆–C₈ alkenols studied in this work with OH and NO₃ radicals, O₃ and Cl atoms.

| Alcohol | τ_{OH} (h) | τ_{NO_3} (h) | τ_{O_3} (h) | τ_{Cl} (h) |
|-------------------|------------------|-------------------|------------------|-----------------|
| (E)-2-hexen-1-ol | 1.4 ^a | 4.3 ^b | — | 81 ^d |
| (E)-3-hexen-1-ol | 1.2 ^a | 1.3 ^b | — | 81 ^d |
| (Z)-3-hexen-1-ol | 1.0 ^a | 2.1 ^b | 6.2 ^c | 95 ^d |
| (Z)-3-hepten-1-ol | — | — | — | 73 ^d |
| (Z)-3-octen-1-ol | — | — | — | 67 ^d |

Superindex letters correspond to the references from which the required rate coefficients were extracted to calculate the corresponding lifetime.

^a Gibilisco et al. (2013).

^b Pfrang et al. (2006).

^c Atkinson (2000).

^d This work. 12 h daylight average OH concentration of $[OH] = 2 \times 10^6$ molecule cm⁻³ (Hein et al., 1997), a 12 h night-time average NO₃ concentration of $[NO_3] = 5 \times 10^8$ molecule cm⁻³ (Atkinson, 2000), a 24 h average O₃ concentration of 7×10^{11} molecule cm⁻³ (Logan, 1985), and an average of chlorine atoms concentration of $[Cl] = 1 \times 10^4$ molecule cm⁻³ (Wingenter et al., 1996).

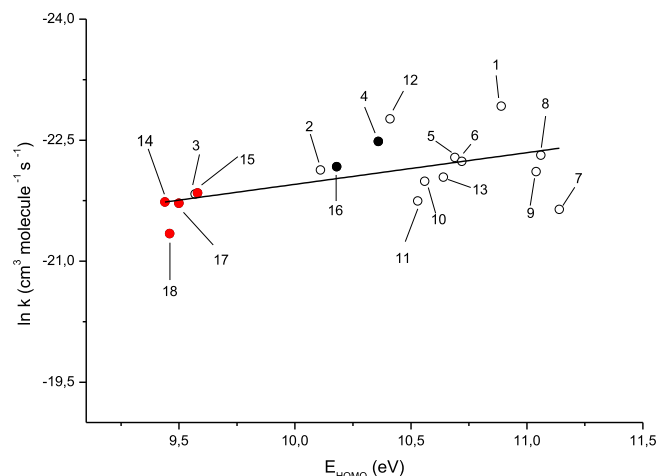


Fig. 2. Correlation plot of $\ln(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ versus calculated E_{HOMO} (eV) for the reactions of Cl atoms with unsaturated VOCs. Red filled circles are unsaturated alcohols from this work (●), alcohols from literature (●) and other unsaturated VOCs from the literature (○). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the formation of thermally stable peroxyacyl nitrates (PANs, RC(O) OONO₂) which are important reservoirs of NO_x and enable its transport throughout the troposphere (Grosjean and Bytnerowicz, 1993; Roberts, 2007). The chemistry of all of these products will play a role in the production of tropospheric ozone and the product studies indicate that they contribute quite significantly to the formation of secondary organic aerosol (Bernard et al., 2012; Noda and Ljungstrom, 2002).

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