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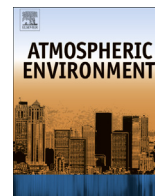


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FTIR gas-phase kinetic study on the reactions of OH radicals and Cl atoms with unsaturated esters: Methyl-3,3-dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate

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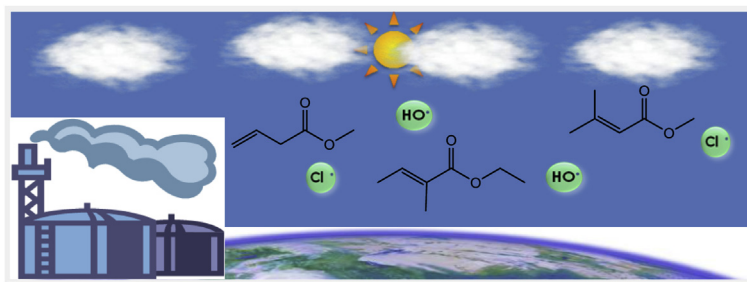
^a Instituto de Investigaciones en Físicoquímica de Córdoba (I.N.F.I.Q.C.), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

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HIGHLIGHTS

- First kinetic data for OH and Cl reactions of nonterminal unsaturated esters.
- Relative kinetics by in situ FTIR spectroscopy at 298 K and 1 atm.
- Reactivity trends in terms of ester and olefinic H substitution.
- Atmospheric lifetimes determined and possible impact assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

The relative-rate technique has been used to obtain rate coefficients for the reactions of the unsaturated esters methyl-3,3-dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate with OH radicals and chlorine atoms at (298 ± 2) K in synthetic air at a total pressure of (760 ± 10) Torr. The experiments were performed in an environmental chamber using in situ FTIR detection to monitor the decay of the esters relative to different reference compounds. The following room temperature rate coefficients (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were obtained: $k_1(\text{OH} + (\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3) = (4.46 \pm 1.05) \times 10^{-11}$, $k_2(\text{Cl} + (\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3) = (2.78 \pm 0.46) \times 10^{-10}$, $k_3(\text{OH} + \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3) = (8.32 \pm 1.93) \times 10^{-11}$, $k_4(\text{Cl} + \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3) = (2.53 \pm 0.35) \times 10^{-10}$, $k_5(\text{OH} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{OCH}_3) = (3.16 \pm 0.57) \times 10^{-11}$, $k_6(\text{Cl} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{OCH}_3) = (2.10 \pm 0.35) \times 10^{-10}$. With the exception of the reaction of Cl with methyl-3,3-dimethyl acrylate (k_2), for which one determination exists in the literature, this study is the first kinetic study for these reactions under atmospheric pressure. Reactivity trends are discussed in terms of the effect of the alkyl and ester groups attached to the double bond on the overall rate coefficients towards OH radicals. The atmospheric implications of the reactions were assessed by the estimation of the tropospheric lifetimes of the title reactions.

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1. Introduction

There are many definitions of the term “volatile organic compounds (VOCs)” and in its broadest sense refers to any organic chemicals found in the atmosphere. VOCs are numerous, varied,

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and ubiquitous at ground level in the atmosphere. They are involved in the formation of tropospheric ozone and secondary organic aerosol (SOA) and play a role in the global greenhouse effect and thus climate change. Apart from the health risks associated with SOA many of the VOCs are themselves directly toxic or possess mutagenic and carcinogenic properties and thus additional dangers to human health. This is particularly true of many α,β -unsaturated esters.

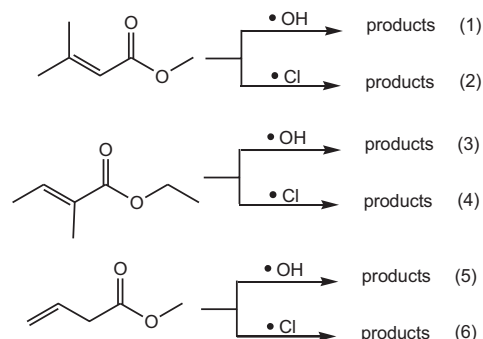
Oxygenated volatile organic compounds (OVOCs) are a class of VOCs possessing oxygen-containing functionalities and are widely emitted into the troposphere by biogenic (mainly vegetation) and anthropogenic (fossil fuel combustion, solvent use, paints, adhesives, etc.) sources (Graedel et al., 1986; Koppmann, 2007). Unsaturated esters are an example of a particular class of anthropogenic OVOC. They are produced industrially by reaction of an acyclic conjugated diolefin with a carboxylic acid in the presence of a catalyst (Lewis, 1975), and are widely used in the production of plastics, resins (Srivastava, 2009), cosmetics, shampoos, toilet soaps and cleaning products.

Widespread use of the esters by industry inevitably results in fugitive emissions of the compounds to the atmosphere. Once in the atmosphere, these OVOCs, like all other VOCs, will be subjected to degradation through reaction with tropospheric oxidants, i.e., mainly with OH radicals during the day, NO₃ radicals during the night and ozone during both day and night. Since the unsaturated esters will be mainly emitted in industrial centers and urban areas their expected relatively fast reactions with tropospheric oxidants due to the presence of the double bond in the compounds will contribute to the ground level ozone and photooxidant formation in areas fairly close to the vicinity of their release.

The atmospheric kinetics and degradation mechanisms of unsaturated esters have not been very extensively investigated. Kinetic studies published to date show that OH radical-initiated photooxidation will mainly determine the atmospheric lifetime of the compounds under most atmospheric conditions (Blanco and Teruel, 2008; Blanco et al., 2006, 2008; Canosa-Mas et al., 1999, 2005; Grosjean and Grosjean, 1998; Grosjean et al., 1993; Martín Porrero et al., 2010; Teruel et al., 2006; Saunders et al., 1994). Although the rate coefficients for the reactions of Cl atoms with VOCs are generally one order of magnitude higher than the corresponding reactions with OH radicals the low global atmospheric concentration of Cl of around 1×10^3 molecule cm⁻³ (Singh et al., 1996) renders Cl atom initiated degradation a minor atmospheric sink for VOCs under most atmospheric conditions. However, in addition, in the marine boundary layer during the early morning hours concentrations of Cl atoms as high as 10^5 atoms cm⁻³ or more have been measured (Spicer et al., 1998; Ezell et al., 2002). In addition, recent field studies in the USA (Thornton et al., 2010), Canada (Mielke et al., 2011) and Germany (Philips et al., 2012) have presented evidence for nitryl chloride (ClNO₂) mediated Cl chemistry in mid-continental regions far removed from coastal and marine regions where it was previously assumed that these were these only regions of the atmosphere in which Cl chemistry was of any significance. The recent field observations suggest that Cl chemistry is potentially more important than previously thought in rural continental regions. Since ClNO₂ is photolabile with a short photolytic lifetime any significant imprint of ClNO₂ driven Cl chemistry will probably be limited to the early morning hours just after dawn when ClNO₂, formed during the night through heterogeneous reactions of N₂O₅ with particle Cl⁻ (Finlayson-Pitts et al., 1989), will be present at appreciable levels.

In this work, we report rate coefficients for the reactions of OH radicals and Cl atoms with three unsaturated esters methyl-3,3-

dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate measured at room temperature and atmospheric pressure using the relative kinetic technique:



This work represents the first measurement of the OH rate coefficients for the title compounds. In the case of the Cl reactions only a rate coefficient for the reaction of Cl with methyl-3,3-dimethyl acrylate of 3.58×10^{-10} cm³ molecule⁻¹ s⁻¹ determined using a relative kinetic method with GC-FID detection of reactants has been reported in the literature (Martín Porrero et al., 2010). The kinetic data reported herein are necessary not only for increasing the kinetic data base on the reactions of unsaturated esters with atmospheric oxidants but also for the realistic representation of the chemistry of these compounds in tropospheric models, which assess their impact on air quality. The results are discussed in terms of the effect that the positions of the methyl substituent, ester functionality and double bond have on the reactivity of different unsaturated esters towards OH radicals. The atmospheric lifetimes of the VOCs studied, with respect to their reactions with OH are calculated with the rate coefficients obtained in this work and compared with the lifetimes of these compounds due to reaction with other tropospheric oxidants.

2. Experimental section

The experiments were performed in a 480 L cylindrical Duran glass vessel (3 m in length, 45 cm in diameter) at (298 ± 2) K and a total pressure of (760 ± 10) Torr synthetic air (760 Torr = 101.325 kPa). The chamber is described in detail elsewhere (Barnes et al., 1993) and only a brief description is given here. The reactor is closed at both ends by aluminium flanges which contain ports for the introduction of bath gases and reactants into the chamber. A mixing fan and a capacitance manometer are also located on the flanges. Arranged concentrically around the outside of the reactor are 20 superactinic lamps (Philips TLA 40W/05, $300 \leq \lambda \leq 450$ nm, $\lambda_{\text{max}} = 360$ nm). The chamber can be evacuated down to 10^{-3} Torr by means of a turbomolecular pump backed by a double stage rotary fore pump. The chamber is equipped with an internally mounted White mirror system operated at an optical path length of 51.6 m which is coupled to an FTIR spectrometer (Nicolet Magna 520) for the acquisition of infrared spectra at a resolution of 1 cm⁻¹.

OH radicals were generated by UV irradiation of methyl nitrite (CH₃ONO) in the presence of NO/O₂, reactions (7)–(9):



Chlorine atoms were generated by photolysis of Cl_2 reaction (10):



Reaction mixtures consisting of an unsaturated ester, a reference organic compound, and the radical precursor, diluted in pure air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 15 min. Known amounts of the reagents were flushed into the reaction chamber in a stream of synthetic air and the reactor was then filled with synthetic air to atmospheric pressure. The reaction mixtures were photolysed for periods of up to 20 min during which time infrared spectra were recorded. Generally, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15 such spectra were recorded per experiment.

In the presence of the oxidant X (OH radical or Cl atom), the ester and reference compounds decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (11) and (12), then it can be shown that:

$$\ln \left\{ \frac{[\text{Ester}]_0}{[\text{Ester}]_t} \right\} = \frac{k_{\text{Ester}}}{k_{\text{Reference}}} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (1)$$

where $[\text{Ester}]_0$, $[\text{Reference}]_0$, $[\text{Ester}]_t$ and $[\text{Reference}]_t$ are the concentrations of the unsaturated ester and reference compound at times $t = 0$ and t , respectively, and k_{Ester} and $k_{\text{Reference}}$ are the rate coefficients of reactions (11) and (12), respectively.

The relative rate technique relies on the assumption that both the unsaturated ester and reference organics are removed solely by reaction with the oxidant species X (OH radicals or Cl atoms). To verify this assumption, various tests were performed to assess possible contributions to the decays of the organics by reaction with the radical precursors CH_3ONO or Cl_2 , photolysis, and loss to the reactor surface. Mixtures containing an unsaturated ester, a reference compound and a radical precursor, either CH_3ONO /NO or Cl_2 , were prepared and allowed to stand in the dark for one hour. In all cases, loss of the organic species, in the presence of the radical precursor and in the absence of UV light, was of negligible showing that both wall deposition and reaction of the organics with the radical precursors are inconsequential loss processes. Additionally, to test for possible photolysis of the organics, mixtures of the organics alone in nitrogen or air were irradiated for 30 min. No photolysis of any of the organics was observed.

The initial concentrations used in the experiments for the unsaturated esters and reference compounds in ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr total pressure) were as follows: ~ 3.9 for methyl-3,3-dimethyl acrylate; ~ 3.7 for (*E*)-ethyl tiglate; ~ 4.8 for methyl-3-butenate; ~ 22.8 for 1-butene and ~ 15.9 for 1,3-butadiene. The concentrations of CH_3ONO , NO and Cl_2 were typically around 22, 11 and 23 ppm, respectively.

The reactants were monitored at the infrared absorption bands centred at the following frequencies (in cm^{-1}): methyl-3,3-dimethyl acrylate at 1159; (*E*)-ethyl tiglate at 1266; methyl-3-butenate at 1176; 1-butene at 912 and 1,3-butadiene at 908.

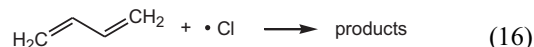
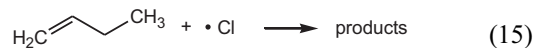
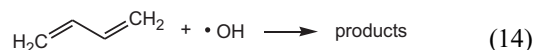
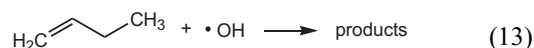
2.1. Materials

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), methyl-3,3-dimethyl acrylate (Aldrich, 97%), (*E*)-ethyl tiglate (Aldrich, >98%), methyl-3-butenate (Aldrich, 95%), 1-butene (Messer Griesheim, 99%), 1,3-butadiene (Aldrich, 99+%), NO (Messer Griesheim, 99%) and Cl_2 (Messer Griesheim, 2.8).

Methyl nitrite was synthesized according to the method of Taylor et al. (1980) by the dropwise addition of 50% H_2SO_4 to a saturated solution of sodium nitrite in methanol and was purified by vacuum distillation.

3. Results

The rate coefficient measurements for the reactions of OH radicals and Cl atoms with methyl-3,3-dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate were each performed relative to two reference compounds: 1-butene and 1,3-butadiene.



where, $k_{13} = (3.14 \pm 0.63) \times 10^{-11}$ (Atkinson, 1986), $k_{14} = (6.93 \pm 0.48) \times 10^{-11}$ (Li et al., 2006), $k_{15} = (3.0 \pm 0.4) \times 10^{-10}$ (Orlando et al., 2003), $k_{16} = (4.2 \pm 0.4) \times 10^{-10}$ (Ragain and Finlayson-Pitts, 1997). All the k values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Representative plots of the kinetic data for these reactions are displayed in Fig. 1. Three experiments were performed for each ester + reference compound + OH (or Cl) combination. The individual rate coefficient ratios ($k_{\text{Ester}}/k_{\text{Reference}}$) determined for each set of experiments are listed in Tables 1 and 2 together with the values of rate coefficients for the reactions of the unsaturated esters with OH radicals and Cl atoms derived from the rate coefficient ratios using the rate coefficients for the reference reactions listed above. The errors for the $k_{\text{Ester}}/k_{\text{Reference}}$ ratios given in Tables 1 and 2 are the 2σ statistical errors from the scatter in the plots shown in Fig. 1. The errors quoted for k_{Ester} are a combination of the 2σ statistical errors from the linear analysis plus the error given in the recommended values of the rate coefficients for the reference reactions.

As can be seen in Fig. 1 good linear plots with zero or near zero intercepts were obtained for the reactions of both OH radicals and Cl atoms with all the unsaturated esters and different reference compounds and reasonable agreement was found between the values of the rate coefficients obtained using the different reference compounds. Since consistent results were obtained using two reference compounds we prefer to give final rate coefficients for the reactions of OH radicals and Cl atoms with the unsaturated esters which are averages of all the determinations for that particular reaction (Tables 1 and 2).

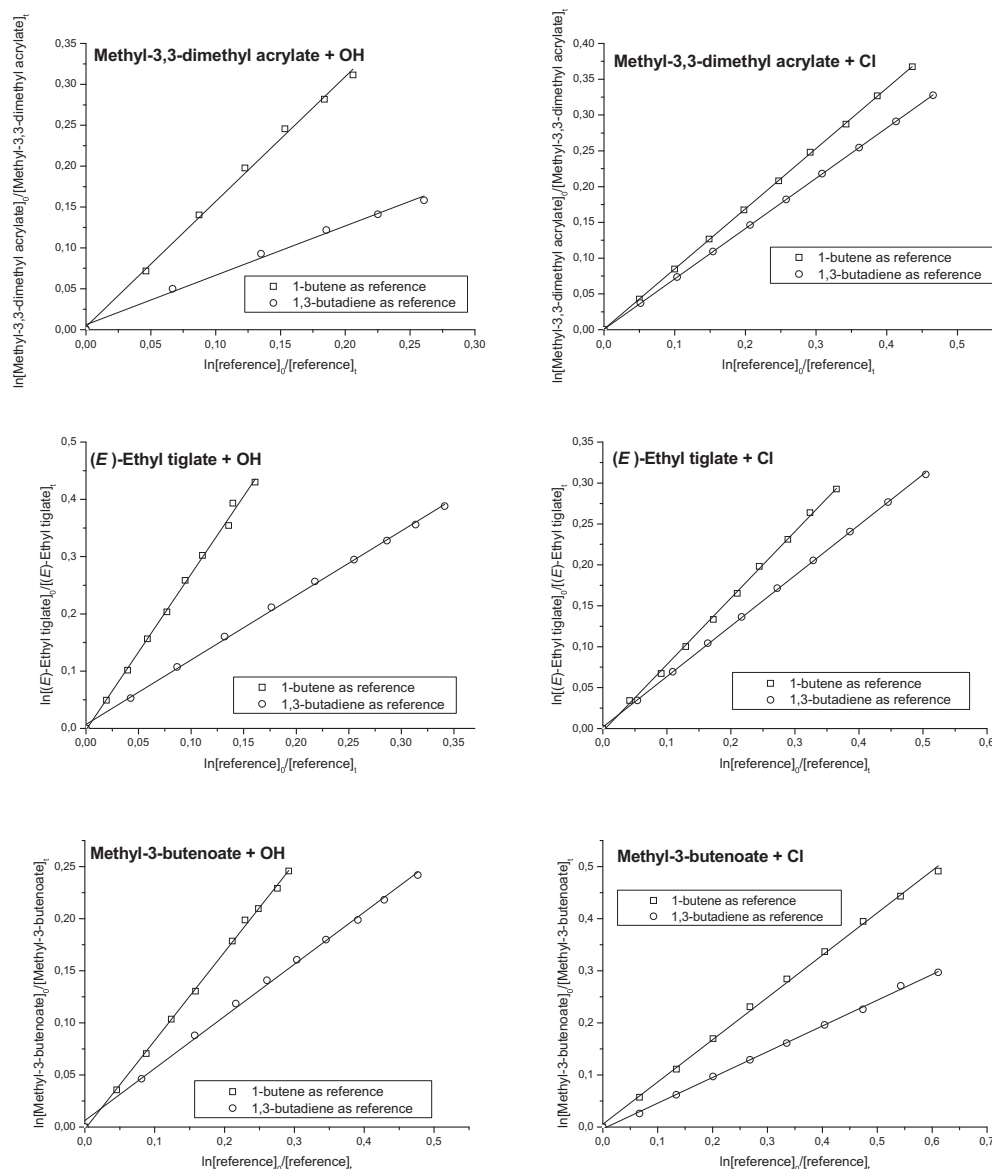


Fig. 1. Exemplary plots of the kinetic data for the reactions of OH and Cl with methyl-3,3-dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate measured relative to the same reactions with the reference compounds 1-butene and butadiene in air at room temperature and atmospheric pressure.

4. Discussion

The measurements reported here constitute the first determination of the rate coefficients for the reactions of OH radicals with methyl-3,3-dimethyl acrylate (k_1), (*E*)-ethyl tiglate (k_3) and methyl-3-butenate (k_5), and of Cl atoms with (*E*)-ethyl tiglate (k_4) and methyl-3-butenate (k_6). The rate coefficient of $k_2 = (2.78 \pm 0.46) \times 10^{-10}$ obtained in this study for the reaction of Cl with methyl-3,3-dimethyl acrylate is in satisfactory agreement, within the experimental errors, with the value of $(3.58 \pm 0.28) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Martín Porrero et al. (2010) also using a relative kinetic method with GC-FID detection.

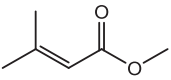
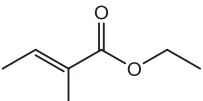
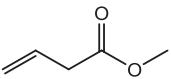
4.1. Reactivity trends

It is interesting to compare the reactivity of methyl-3,3-dimethyl acrylate, (*E*)-ethyl tiglate and methyl-3-butenate towards OH radicals with that of other unsaturated esters and alkenes, since they will react in an analogous manner with OH, i.e.

largely by addition of OH to the double bond in the compounds with the other possible reaction pathway, abstraction of H-atoms by OH, only playing a minor role (Mellouki et al., 2003; Atkinson and Arey, 2003). Table 3 lists the room temperature rate coefficients of the reactions of OH radicals with the unsaturated esters studied in this work, together with available literature rate coefficients for other unsaturated esters. Also shown in Table 3 are the rate coefficients for the reactions of OH for the alkenes corresponding to i) replacement of the ester moiety with an H-atom and ii) replacement of the ester moiety with the ester alkyl group. In cases where a rate coefficient for an analogous alkene was not available rate coefficients are given for the closest possible alternative.

As can be seen in Table 3, both the alkenes and the unsaturated esters generally show an increase in reactivity towards electrophilic attack by the OH radical with increasing methyl substitution at the double bond due to the positive inductive effect of these groups, for example, for the unsaturated esters (in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3} = 8.32 > k_{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3} = 4.96 >$

Table 1Measured rate coefficient ratios, $k_{\text{Ester}}/k_{\text{Reference}}$, and the rate coefficients for the reactions of OH with the unsaturated esters at (298 ± 2) K derived from these ratios.

Ester	Reference	$k_{\text{Ester}}/k_{\text{Reference}}$	k_{Ester} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
 Methyl-3,3-dimethyl acrylate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	1.57 ± 0.02	$(4.86 \pm 1.04) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	1.53 ± 0.03	$(4.72 \pm 1.05) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	1.53 ± 0.04	$(4.69 \pm 1.05) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.60 ± 0.02	$(4.19 \pm 0.46) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.60 ± 0.03	$(4.15 \pm 0.47) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.60 ± 0.02	$(4.12 \pm 0.42) \times 10^{-11}$
	Average		$(4.46 \pm 1.05) \times 10^{-11}$
 (E)-Ethyl tiglate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	2.72 ± 0.05	$(8.38 \pm 1.84) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	2.99 ± 0.02	$(9.18 \pm 1.93) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	2.82 ± 0.02	$(8.65 \pm 1.81) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	1.13 ± 0.01	$(7.81 \pm 0.63) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	1.15 ± 0.01	$(7.95 \pm 0.64) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	1.15 ± 0.01	$(7.95 \pm 0.64) \times 10^{-11}$
	Average		$(8.32 \pm 1.93) \times 10^{-11}$
 Methyl-3-butenolate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.85 ± 0.01	$(2.64 \pm 0.56) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.86 ± 0.01	$(2.67 \pm 0.57) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.88 ± 0.01	$(2.70 \pm 0.57) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.50 ± 0.01	$(3.47 \pm 0.30) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.54 ± 0.01	$(3.77 \pm 0.31) \times 10^{-11}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.53 ± 0.01	$(3.69 \pm 0.30) \times 10^{-11}$
	Average		$(3.16 \pm 0.57) \times 10^{-11}$

$k_{\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3} = 1.70$. The only exception for the esters is the reaction of OH with the dimethylated double bond, methyl-3,3-dimethyl acrylate ($(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3$), which shows almost the same reactivity towards OH ($k_{(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3} = 4.46 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) as esters containing only one methyl group ($k_{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3} = 4.65 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3} = 4.20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). A possible reason for this apparent reduced reactivity toward OH radical addition is discussed below.

In the esters listed in Table 3 the contribution of H-atom abstraction from the methyl and ethyl groups in the ester moieties by the OH radical is estimated to be around 0.22×10^{-12} and $1.49 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Kwok and Atkinson, 1995), i.e. the process will not contribute more than a few percent to the overall measured rate coefficient. Inspection of Table 3 shows that the rate coefficients for OH with the unsaturated esters where

the ester moiety is attached to the double are all higher than the OH rate coefficients for the alkenes resulting from replacement of the ester moiety with an H-atom. The only exception again is the rate coefficient for OH with methyl-3,3-dimethyl acrylate ($k_{(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3} = 4.46 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) which is very close to that of OH with isobutene (2-methylpropene, $k_{(\text{CH}_3)_2\text{C}=\text{CH}_2} = 4.20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The presence of a $-\text{C}(\text{O})\text{OR}$ group attached to the double bond is apparently exerting an activating effect on the bond toward electrophilic addition reactions (Table 3). Blanco et al. (2012) have also noted unexpectedly high reactivity of unsaturated ketones toward OH in which the CO group is directly attached to the double bond. To explain their observations they suggested that the mechanism of OH radical addition in the unsaturated ketones may be different to that of alkyl substituted alkenes and could potentially involve formation of a hydrogen-bonded complex between OH and the

Table 2Measured rate coefficient ratios, $k_{\text{Ester}}/k_{\text{Reference}}$, and the rate coefficients for the reactions of Cl with the unsaturated esters at (298 ± 2) K derived from these ratios.

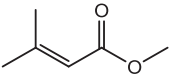
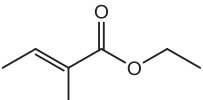
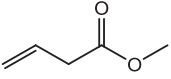
Ester	Reference	$k_{\text{Ester}}/k_{\text{Reference}}$	k_{Ester} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
 Methyl-3,3-dimethyl acrylate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.95 ± 0.03	$(2.86 \pm 0.46) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.88 ± 0.03	$(2.63 \pm 0.36) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.84 ± 0.02	$(2.53 \pm 0.34) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.70 ± 0.01	$(2.96 \pm 0.28) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.70 ± 0.01	$(2.96 \pm 0.29) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.65 ± 0.01	$(2.75 \pm 0.27) \times 10^{-10}$
	Average		$(2.78 \pm 0.46) \times 10^{-10}$
 (E)-Ethyl tiglate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.81 ± 0.01	$(2.44 \pm 0.35) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.85 ± 0.01	$(2.54 \pm 0.35) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.79 ± 0.01	$(2.38 \pm 0.33) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.62 ± 0.01	$(2.59 \pm 0.26) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.63 ± 0.01	$(2.66 \pm 0.27) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.60 ± 0.01	$(2.54 \pm 0.25) \times 10^{-10}$
	Average		$(2.53 \pm 0.35) \times 10^{-10}$
 Methyl-3-butenolate	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.81 ± 0.01	$(2.44 \pm 0.35) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.73 ± 0.01	$(2.19 \pm 0.30) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.70 ± 0.01	$(2.11 \pm 0.31) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.49 ± 0.01	$(2.07 \pm 0.22) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.46 ± 0.01	$(1.90 \pm 0.20) \times 10^{-10}$
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.45 ± 0.01	$(1.89 \pm 0.19) \times 10^{-10}$
	Average		$(2.10 \pm 0.35) \times 10^{-10}$

Table 3

Comparison of the rate coefficients at atmospheric pressure and 298 K for the reactions of different alkenes, $\text{CH}_2=\text{CHR}$, with OH radicals with those for unsaturated esters. Unless specified, in cases where E- and Z-isomers are possible the esters are a mixture of the isomers.

Alkene	k_{OH} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Ester	k_{OH} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{CH}_2=\text{CH}_2$	$0.85 \times 10^{-11\text{a}}$	$\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$	$1.30 \times 10^{-11\text{b}}$
$\text{CH}_2=\text{CHCH}_3$	$2.63 \times 10^{-11\text{a}}$		
$\text{CH}_2=\text{CH}_2$	$0.85 \times 10^{-11\text{a}}$	$\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$	$1.70 \times 10^{-11\text{b}}$
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	$3.14 \times 10^{-11\text{a}}$		
$\text{CH}_3\text{CH}=\text{CH}_2$	$2.63 \times 10^{-11\text{a}}$	$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$	$4.65 \times 10^{-11\text{c}}$
E- $\text{CH}_3\text{CH}=\text{CHCH}_3$	$6.40 \times 10^{-11\text{a}}$		
Z- $\text{CH}_3\text{CH}=\text{CHCH}_3$	$5.64 \times 10^{-11\text{a}}$		
$\text{CH}_3\text{CH}=\text{CH}_2$	$2.63 \times 10^{-11\text{a}}$	$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$	$4.96 \times 10^{-11\text{c}}$
E- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$	$6.70 \times 10^{-11\text{a}}$		
Z- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$	$6.50 \times 10^{-11\text{a}}$		
$\text{CH}_3\text{CH}_2=\text{CH}_2$	$2.63 \times 10^{-11\text{a}}$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$	$4.20 \times 10^{-11\text{b}}$
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	$5.14 \times 10^{-11\text{a}}$		
$\text{CH}_3\text{CH}=\text{CH}_2$	$2.63 \times 10^{-11\text{a}}$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$	$4.58 \times 10^{-11\text{d}}$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$6.10 \times 10^{-11\text{a}}$		
E- $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_3)$	$6.40 \times 10^{-11\text{a}}$	E- $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$	$8.32 \times 10^{-11\text{e}}$
$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$	^f		
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$5.14 \times 10^{-11\text{a}}$	$(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3$	$4.46 \times 10^{-11\text{e}}$
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$8.90 \times 10^{-11\text{a}}$		
$\text{CH}_3\text{CH}=\text{CH}_2$	$2.63 \times 10^{-11\text{a}}$	$\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{OCH}_3$	$3.16 \times 10^{-11\text{e}}$
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	$3.14 \times 10^{-11\text{a}}$		

^a Atkinson and Arey, 2003.

^b Teruel et al., 2006.

^c Teruel et al., 2012.

^d Blanco et al., 2006.

^e This work.

^f Rate coefficients are not available in the literature for 3-methyl-2-pentene.

carbonyl group with resonance effects between the ester and alkene entities possibly also playing an activating role. The higher than expected rate coefficients obtained for the reactions of OH with unsaturated ester groups, where the ester group is directly attached to the double bond reported here and in the literature, would support that such a similar mechanism is probably also operative for these compounds. This seems to follow the reactivity pattern observed in the condensed phase. In general, the radical addition to conjugated systems α,β -unsaturated ketones, esters or nitriles proceed in a regioselective manner affording the radical intermediate stabilized by resonance by the carbonyl, ester or nitrile group (Smith and March, 2007).

Further inspection of Table 3 shows that the rate coefficients for the reactions of OH with the esters are in most cases smaller than those for the reaction of OH with the alkenes obtained on replacement of the ester group with the ester alkyl group. For example, the rate constants (in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3} = 1.30 < k_{\text{CH}_2=\text{CHCH}_3} = 2.63$; $k_{(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3} = 4.46 < k_{(\text{CH}_3)_2\text{C}=\text{CHCH}_3} = 8.90$.

Finally, making a comparison between the rate coefficient (in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$ (4.65) or $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$ (4.96) with $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3$ (4.46) no change in the stability (reactivity) of the double bond is seen on adding an additional CH_3 group on carbon 3. This can be attributed to a possible steric hindrance on carbon 3 in the $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3$. Because of this, it can be proposed that the

addition reaction with the OH radical, takes place on carbon 2, that has less nucleophilic character, due to the presence of the $\text{C}(\text{O})\text{OCH}_3$ group. This fact, can explain the reason of the similar kinetic constant observed for these compounds. On the other hand, if the additional CH_3 group is on carbon 2 as in E- $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$, the kinetic constant rises due to the increase on the electron density in the double bond. A possible explanation is, that in this case, after the addition reaction of OH radical to the double bond, the new radical centre formed has an additional stabilization due to a synergic effect generated by the presence of an electron-withdrawing ($-\text{C}(\text{O})\text{OCH}_2\text{CH}_3$) and an electron donor group ($-\text{CH}_3$) (Viehe et al., 1979; Baldock et al., 1974). For example (rate coefficients in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3} = 8.32 > k_{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3} = 4.58$ or $k_{\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3} = 4.65$ or $k_{(\text{CH}_3)_2\text{C}=\text{CHC}(\text{O})\text{OCH}_3} = 4.46$.

Unfortunately insufficient kinetic data are available on the OH reactivities of the corresponding unsaturated aldehyde and ketone analogues to allow a meaningful comparison with the OH reactivities of the unsaturated esters to be made.

In the case of methyl-3-butenate (4.65) where a $-\text{CH}_2-$ group separates the ester group from the double bond very little influence of the ester group occurs and the reactivity of the compound toward OH is as expected very similar to that of 1-butene ($k = 3.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

4.2. Atmospheric implications

The contribution of OH radicals and Cl atoms to the atmospheric oxidation of methyl-3,3-dimethyl acrylate, (E)-ethyl tiglate and methyl-3-butenate can be assessed by estimating the lifetimes of these unsaturated esters with respect of the reaction with each oxidant. Unfortunately, no data are available on the reactions of O_3 molecules and NO_3 radicals with these unsaturated esters.

Tropospheric lifetimes were calculated using the expression: $\tau_x = 1/k_x[\text{X}]$ with $\text{X} = \text{OH}$ and Cl , where k_x is the rate coefficient for the reaction of the oxidant X with the unsaturated ester and $[\text{X}]$ is the typical atmospheric concentration of the oxidant. The rate coefficients obtained in this work have been used in combinations

Table 4

Calculated atmospheric lifetimes of methyl-3,3-dimethyl acrylate, (E)-ethyl tiglate and methyl-3-butenate for reaction with OH radicals and Cl atoms.

Ester	k_{OH}^{a} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	τ_{OH} (h)	k_{Cl}^{a} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	τ_{Cl} (days)
Methyl-3,3-dimethyl acrylate	4.46×10^{-11}	3.1	2.78×10^{-10}	4.2
(E)-ethyl tiglate	8.32×10^{-11}	1.7	2.53×10^{-10}	4.6
Methyl-3-butenate	3.16×10^{-11}	4.4	2.10×10^{-10}	5.5

^a This work.

with a 12 h daytime average global tropospheric OH radical concentration of $[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$ (Hein et al., 1997), and chlorine atoms concentration of $[\text{Cl}] = 1 \times 10^4 \text{ atoms cm}^{-3}$ (Wingenter et al., 1996) for the calculations. The estimated tropospheric lifetimes at room temperature of the unsaturated esters with the tropospheric oxidants OH and Cl, are listed in Table 4.

Photolytic loss of the unsaturated esters will be negligible since they are photolytically stable in the actinic region of the electromagnetic spectrum. As mentioned above, no data are available on the reactions of NO_3 radicals or O_3 molecules with these unsaturated esters, however, on the basis of structural similarities it is probable that they will show a similar reactivity toward O_3 as other unsaturated esters and thus will have a similar lifetime with respect to reaction with this oxidant. As can be seen in Table 4, the reaction with OH radical is the major loss process for the unsaturated esters studied. These lifetimes, in the range of few hours, indicate that the VOCs are likely to be removed rapidly in the gas phase and degraded near to their emissions sources.

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