

# The Cl-initiated oxidation of $\text{CH}_3\text{C}(\text{O})\text{OCH}=\text{CH}_2$ , $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ , and $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$ in the troposphere

María B. Blanco · Justinian Bejan · Ian Barnes ·  
Peter Wiesen · Mariano A. Teruel

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## Abstract

**Background, aim, and scope** Unsaturated esters are emitted to the atmosphere from biogenic and anthropogenic sources, including those from the polymer industry. Little information exists concerning the atmospheric degradation of unsaturated esters, which are mainly initiated by OH radicals. Limited information is available on the degradation of alkenes by Cl atoms and almost no data exists for the reactions of unsaturated esters with Cl atoms. This data is necessary to assess the impact of such reactions in maritime environments where, under circumstances, OH radical- and Cl atom-initiated oxidation of the compounds can be important. Rate coefficients for the reactions of chlorine atoms with vinyl acetate, allyl acetate, and *n*-butyl acrylate have been determined at  $298 \pm 3$  K and atmospheric pressure. The kinetic data have been used in combination with that for structurally similar compounds to infer the kinetic contributions from the possible reaction channels to the overall reaction rate.

**Materials and methods** The decay of the organics was followed using in situ Fourier transform infrared spectroscopy and the rate coefficients were determined using a relative kinetic method and different hydrocarbon reference compounds.

**Results** The following room temperature rate coefficients (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) were obtained:  $k_1$  ( $\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{OCH}=\text{CH}_2$ ) =  $(2.68 \pm 0.91) \times 10^{-10}$ ,  $k_2$  ( $\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ ) =  $(1.30 \pm 0.45) \times 10^{-10}$ , and  $k_3$  ( $\text{Cl} + \text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$ ) =  $(2.50 \pm 0.78) \times 10^{-10}$ , where the uncertainties are a combination of the  $2\sigma$  statistical errors from linear regression analyses and a contribution to cover uncertainties in the rate coefficients of the reference hydrocarbons.

**Discussion** This is the first kinetic study of the title reactions under atmospheric conditions. The kinetic data were analyzed in terms of reactivity trends and used to estimate the atmospheric lifetimes of the esters and assess their potential importance in the marine atmosphere.

**Conclusions** Although reaction with OH radicals is the major atmospheric sink for the unsaturated esters studied, reaction with Cl atoms can compete in the early morning hours in coastal areas where the Cl concentration can reach peak values as high as  $1 \times 10^5$  atoms  $\text{cm}^{-3}$ . The calculated residence times show that the chemistry of unsaturated esters will impact air quality locally near their emission sources.

**Recommendations and perspectives** The reactions need to be studied over the range of temperatures and pressures generally encountered in the marine atmosphere. In addition, product studies should also be performed as a function of temperature since this will allow degradation mechanisms to be derived, which are representative for the wide range of conditions occurring in marine

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M. B. Blanco · M. A. Teruel (✉)  
Instituto de Investigaciones en Físicoquímica de Córdoba (I.N.F.I. Q.C.), Dpto. de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina  
e-mail: mteruel@fcq.unc.edu.ar

I. Bejan · I. Barnes · P. Wiesen  
FB C—Physikalische Chemie, Bergische Universität Wuppertal, 42097 Wuppertal, Germany

I. Bejan  
Faculty of Inorganic and Analytical Chemistry,  
'Al. I. Cuza' University of Iasi,  
Iasi, Romania

environments. Inclusion of the kinetic and product data in tropospheric numerical models will allow an assessment of potential environmental impacts of the esters for different marine pollution scenarios.

**Keywords** Chlorine atoms · Environmental chamber · Rate coefficients · Tropospheric chemistry · Unsaturated esters

## 1 Background, aim, and scope

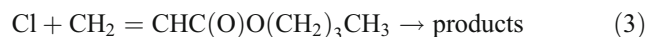
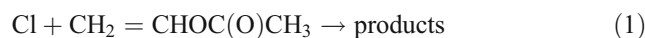
Acetates are emitted to the atmosphere from vegetation and through their use in industry (Helmig et al. 1989). Another potential source is emission from automobiles; a number of acetates, including VAC ( $\text{CH}_3\text{C}(\text{O})\text{OCH}=\text{CH}_2$ ) and AAC ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ ), have been detected as products in the combustion of rape methyl esters used as fuel alternatives or additives (Ferrari 1995). Acrylate esters containing a double bond and functional carboxyl group are used chiefly as a monomer or co-monomer in making acrylic and modacrylic fibers. They are used in formulating paints and dispersions for paints, inks, and adhesives, in making cleaning products, antioxidant agents, amphoteric surfactants as well as in making aqueous resins and dispersions for textiles and papers. BUAC ( $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$ ) is a very useful feedstock for chemical syntheses, because it readily undergoes addition reactions with a wide variety of organic and inorganic compounds.

Once in the atmosphere, these volatile organic compounds (VOCs) react with tropospheric oxidants, i.e., mainly with OH radicals during the day and  $\text{NO}_3$  radicals and ozone during the night. These reactions contribute to tropospheric ozone and photooxidant formation in urban areas. Chlorine atoms, present at an average global concentration of about  $1 \times 10^4$  atoms  $\text{cm}^{-3}$  (Wingenter et al. 1996), can also play an important role in atmospheric chemistry since atomic Cl usually reacts with organic compounds (VOCs) much faster than OH radicals. Moreover, in the marine boundary layer during the early morning hours, the concentration of Cl atoms is estimated to be significantly large, as high as  $10^5$  atoms  $\text{cm}^{-3}$  or more (Spicer et al. 1998; Ezell et al. 2002). Thus, reactions with chlorine atoms in coastal areas may represent a significant loss process for VOCs at specific times of the day.

In order to assess the possible impact of the reactions of Cl atoms with VOCs on air quality, kinetic and mechanistic information on their tropospheric degradation is needed.

We report here room temperature atmospheric pressure measurements of rate coefficients for the reactions of Cl

atoms with VAC ( $k_1$ ), AAC ( $k_2$ ), and BUAC ( $k_3$ ) performed in a large volume photoreactor:



To the best of our knowledge, rate coefficients for the reactions of Cl atoms with the three esters have not been reported previously in the literature. The aim of the work is to achieve a better understanding of the reactivity of  $\alpha,\beta$ -unsaturated oxygenated VOCs toward OH radicals and Cl atoms and is an extension of previous work on the reactivity of OH toward unsaturated esters (Teruel et al. 2006; Blanco et al. 2006; Blanco and Teruel 2008) and OH and Cl toward acrylic acid and acrylonitrile (Teruel et al. 2007). In conjunction with other available kinetic data, the results are discussed in terms of the substituent effects on the reactivity of the olefinic carbons toward Cl atoms and complements our previous reactivity studies (Blanco et al. 2006; Teruel et al. 2007; Blanco et al. 2008).

## 2 Experimental and materials

### 2.1 Experimental system

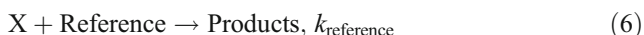
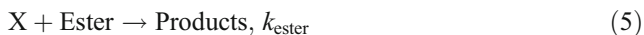
All the experiments were performed in a 1,080  $\text{dm}^3$  quartz-glass reaction chamber at a total pressure of 760 Torr (760 Torr=101.325 kPa) and  $298 \pm 3$  K in synthetic air. A detailed description of the reactor can be found elsewhere (Barnes et al. 1994) and only a brief description is given here. A pumping system consisting of a turbomolecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to  $10^{-3}$  Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 super-actinic fluorescent lamps (Philips TL05 40W; 320–480 nm,  $\lambda_{\text{max}}=360$  nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White-type multiple-reflection mirror system with a base length of  $5.91 \pm 0.01$  m for sensitive in situ long path absorption monitoring of reactants and products in the IR spectral range 4,000–700  $\text{cm}^{-1}$ . The White system was operated at 82 traverses, giving a total optical path length of  $484.7 \pm 0.8$  m. The IR spectra were

recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Nicolet Nexus FT-IR spectrometer, equipped with a liquid nitrogen cooled mercury–cadmium–tellurium detector. Typically, for each spectrum, 64 interferograms were co-added over 1 min and 15 such spectra were recorded per experiment.

Chlorine atoms were generated by the photolysis of Cl<sub>2</sub> with the fluorescent lamps:



In the presence of Cl atoms, the esters and the references decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (5) and (6), then it can be shown that:

$$\ln \left\{ \frac{[\text{Ester}]_0}{[\text{Ester}]_t} \right\} = \frac{k_{\text{ester}}}{k_{\text{reference}}} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (7)$$

where [Ester]<sub>0</sub>, [Reference]<sub>0</sub>, [Ester]<sub>t</sub>, and [Reference]<sub>t</sub> are the concentrations of the esters and reference compound at times *t*=0 and *t*, respectively, and *k*<sub>ester</sub> and *k*<sub>reference</sub> are the rate coefficients of reactions (5) and (6), respectively.

The relative rate technique relies on the assumption that both the ester and reference organics are removed solely by reaction with Cl atoms. To verify this assumption, various tests were performed to assess the loss of the reactants via reaction with molecular chlorine, photolysis, and wall deposition. Reaction with molecular chlorine and photolysis was found to be negligible for BUAC and the reference compounds, although some wall loss was observed for VAC and AAC. This wall loss was measured prior to switching on the photolysis lamps and the following modified version of Eq. (7) was used in the kinetic analysis:

$$\ln \left\{ \frac{[\text{Ester}]_0}{[\text{Ester}]_t} \right\} - k_{\text{wall}}(t - t_0) = \frac{k_{\text{ester}}}{k_{\text{reference}}} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (8)$$

where *k*<sub>wall</sub> is the first order wall loss rate coefficient of the ester.

The initial concentrations of reactants in ppmV (1 ppmV=2.46×10<sup>13</sup> molecule cm<sup>-3</sup> at 298 K) were: vinyl acetate (VAC) 0.3–0.6; allyl acetate (AAC) 0.6–0.9; *n*-butyl acrylate (BUAC) 0.6–0.8; Cl<sub>2</sub>, 4.6; isobutene 1.4–1.9; and 1,3-butadiene 0.9–1.0.

The reactants were monitored at the following infrared absorption frequencies (in cm<sup>-1</sup>): vinyl acetate at 1,148;

allyl acetate at 1,238; butyl acrylate at 1,194.5; isobutene at 890; and 1,3-butadiene at 908.4.

### 3 Materials

The following chemicals with purities as stated by the supplier were used without further purification: synthetic air (Air Liquide, 99.999%), vinyl acetate (Aldrich, 99%), allyl acetate (Aldrich, 99%), butyl acrylate (Aldrich, 99%), isobutene (Messer Griesheim, 99%), 1,3-butadiene (Aldrich, 99+%), and Cl<sub>2</sub> (Messer Griesheim, 2.8).

### 4 Results and discussion

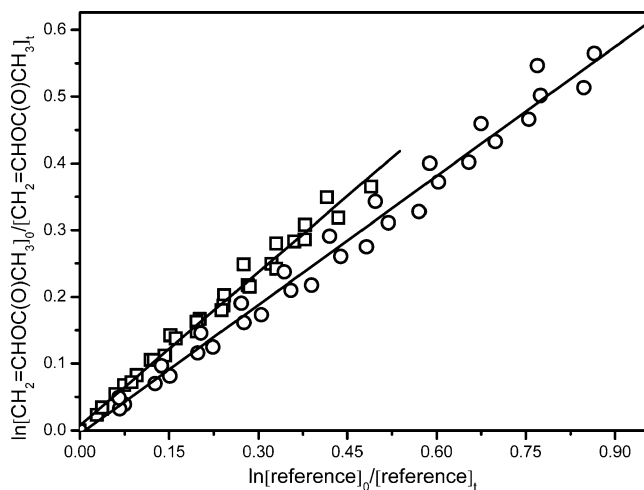
#### 4.1 Kinetic conditions and results

Rate coefficients for the reactions of Cl atoms with vinyl acetate, allyl acetate, and butyl acrylate were determined by comparing their rate of decay with that of the corresponding decay of the reference compounds. Mixtures of the esters and reference compounds with Cl<sub>2</sub> were stable in the dark when left in the chamber for the typical time span of the kinetic experiments (10–20 min). Moreover, in the absence of Cl<sub>2</sub>, photolysis of the mixtures (esters and reference compounds in air) did not show any decrease in the reactant concentrations over the time span of the experiments.

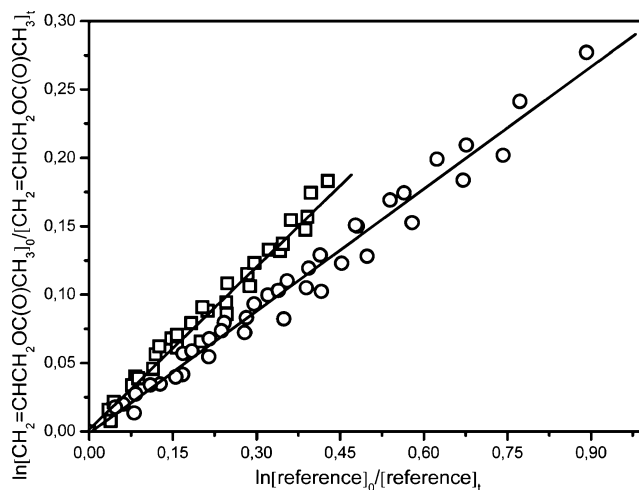
Figures 1, 2, and 3 show the kinetic data obtained from the experiments plotted according to Eq. (7) (or Eq. 8, to account for wall losses) for the reactions of Cl with the individual esters measured relative to different reference compounds. Each plot represents a minimum of three experiments. Good linear relationships were obtained in all cases. The linearity of the plots with practically zero intercepts combined with the fact that similar results were obtained for different initial concentrations of the esters and reference organics supports that complications due to secondary reactions in the experimental systems were negligible.

The *k*<sub>ester</sub>/*k*<sub>reference</sub> ratios determined from the slopes of the straight-line plots in Figs. 1, 2, and 3 are listed in Table 1 together with the absolute values of the rate coefficients, *k*<sub>ester</sub>, calculated from the *k*<sub>ester</sub>/*k*<sub>reference</sub> ratios.

In order to put the rate coefficients for the reactions of Cl with the esters on an absolute basis, the following values for the reactions of Cl with the reference compounds at 298 K were used: (3.40±0.28)×10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for Cl + isobutene (Ezell et al. 2002) and (4.2±0.4)×10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for Cl+1,3-butadiene (Ragains et al. 1997). The errors for the ratios *k*<sub>ester</sub>/*k*<sub>reference</sub> are only 2σ statistical errors. The errors quoted for *k*<sub>ester</sub> in Table 1 are a combination of the 2σ statistical errors from the linear



**Fig. 1** Plots of the kinetic data for the reaction of VAC with Cl atoms using isobutene ( $\square$ ) and 1,3-butadiene ( $\circ$ ) as reference hydrocarbons



**Fig. 2** Plots of the kinetic data for the reaction of AAC with Cl atoms using isobutene ( $\square$ ) and 1,3-butadiene ( $\circ$ ) as reference hydrocarbons

regression analysis plus an additional 20% error to cover potential uncertainties in the recommended values of the rate coefficients for the reference reactions. The corrections for wall deposition of VAC and AAC were approximately 20–35%.

For all the esters, there is a good agreement between the values of  $k_{\text{ester}}$  determined using two different reference compounds. We therefore prefer to quote rate coefficients for the reactions of Cl with the esters, which are averages of the determinations using both reference compounds. Averaging the values of the rate coefficients and taking errors which encompass the extremes of both determinations for each reaction results in the following values for the reaction rate coefficients at 298 K (listed as  $k_{\text{average}}$  in Table 1):

$$k_{\text{Cl+VAC}} = (2.68 \pm 0.91) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{Cl+AAC}} = (1.30 \pm 0.45) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

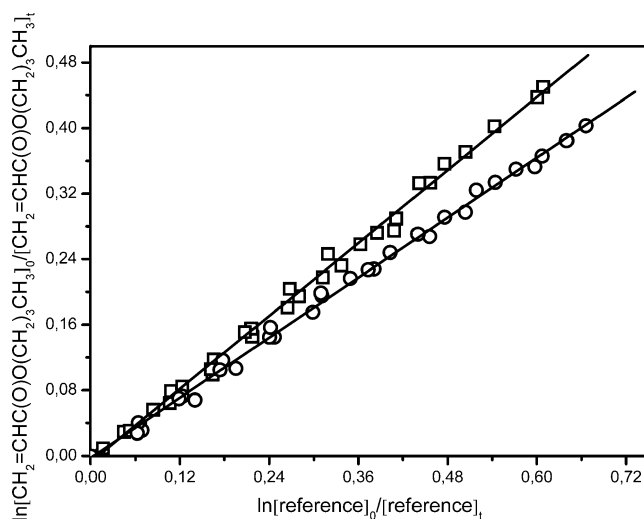
$$k_{\text{Cl+BUAC}} = (2.50 \pm 0.78) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To the best of our knowledge, this is the first report of room temperature rate coefficients for the reaction of Cl atoms with VAC, AAC, and BUAC and, therefore, no direct comparison with literature data can be made.

#### 4.2 Reactivity trends

In Table 2, the room temperature rate coefficients obtained for the reactions of Cl with VAC, AAC, and BUAC are compared with those for the reactions of Cl atoms with structurally similar compounds. Although all the reactions are fast comparisons between the rate coefficients can be used to infer the influence of the different functional groups on the kinetics and also the relative contributions of the available reaction channels to the overall reaction. The present work has

shown that the rate coefficient for the reaction of Cl with VAC ( $2.68 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is a factor of 2 higher than that of Cl with AAC ( $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The higher rate coefficient for Cl with VAC compared to Cl with AAC can be attributed to the activation of the double bond toward Cl addition by the conjugation effect of the lone pair electrons on the O atom of the VAC ester group with the olefinic  $\pi$  electron system. In the case of AAC, this conjugation is not possible due to the  $-\text{CH}_2-$  entity that separates the O atom from the olefinic  $\pi$  system. Generally, oxygen atoms can activate more efficiently than  $\text{CH}_3$  groups, although, in this particular case, the rate coefficient for the reaction of



**Fig. 3** Plots of the kinetic data for the reaction of BUAC with Cl atoms using isobutene ( $\square$ ) and 1,3-butadiene ( $\circ$ ) as reference hydrocarbons

**Table 1** Rate coefficient ratio  $k_{\text{ester}}/k_{\text{reference}}$  and rate coefficients for the reactions of Cl atoms with vinyl acetate (VAC), allyl acetate (AAC), and butyl acrylate (BUAC) at  $298\pm 3$  K in  $760\pm 10$  Torr of air

Reactant	Reference	$k_{\text{ester}}/k_{\text{reference}}$	$k_{\text{ester}}$ $10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$k_{\text{average}}$ $10^{-10}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
VAC	Isobutene	0.79±0.03	2.69±0.64	2.68±0.91
	1,3-Butadiene	0.64±0.03	2.67±0.65	
AAC	Isobutene	0.40±0.02	1.36±0.33	1.30±0.45
	1,3-Butadiene	0.29±0.01	1.24±0.30	
BUAC	Isobutene	0.72±0.02	2.46±0.55	2.50±0.78
	1,3-Butadiene	0.61±0.01	2.54±0.56	

Cl with VAC is very similar to that for Cl with propene, where the double bond is activated toward Cl addition by the positive inductive effect of the methyl group.

The rate coefficient for Cl with AAC is also much lower than those of Cl with propene and *n*-butene indicating a complete lack of any inductive effect from a  $-\text{CH}_2-$  group adjacent to a  $-\text{C}(\text{O})\text{O}$  moiety. In fact, the reactivity of Cl toward AAC is only slightly higher than that of Cl toward ethene. Rodriguez et al. (2007) have reported a rate coefficient of  $1.72\pm 0.19\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction of Cl with allyl alcohol ( $\text{CH}_2=\text{CHCH}_2\text{OH}$ ) at 298 K and atmospheric pressure. The observations suggest that the  $-\text{CH}_2\text{CH}=\text{CH}_2$  unit in AAC has a reactivity toward Cl atoms very similar to that of Cl toward  $\text{CH}_2=\text{CHCH}_2\text{OH}$ .

Ezell et al. (2002) have shown that allylic hydrogen atoms react less rapidly with Cl atoms than the analogous alkyl hydrogens in alkanes. From fits of kinetic data, estimations have been made of the rates of allylic H-atom abstraction from alkenes. If this data is transferable to the present vinyl acetates, one would expect a rate coefficient contribution of around  $4.0\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ezell et al. 2002) for abstraction of the allylic hydrogens from the  $-\text{CH}_2\text{CH}=\text{CH}_2$  group in AAC. Aranda et al. (2003) in a low pressure study have proposed a rate coefficient  $2.9\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the abstraction channel in the reaction of Cl with allyl alcohol, which agrees fairly well with the value estimated here for AAC. Taking the rate coefficient measured in this work for Cl with AAC, this would imply a rate coefficient contribution of around  $0.9\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for Cl addition to the double bond, i.e., this suggests that the double bond in AAC is exhibiting a reactivity toward Cl-atom addition similar to that observed for Cl with ethene and that addition will be the major reaction pathway. Alternately, one could consider that the reactivity of the  $-\text{OCH}_2-$  group in  $-\text{OCH}_2\text{CH}=\text{CH}_2$  will not be much different to that of the  $-\text{OCH}_2-$  groups in simple alkyl acetates where the reaction of Cl with ethyl acetate would suggest a value of around  $2\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the abstraction. This approach gives a value of  $1.1\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

for the addition of to the double bond. Both approaches lead to the conclusion that Cl addition to the double bond in AAC dominates the reaction mechanism with a contribution of between 70% and 85%.

Vinyl acetate ( $\text{CH}_3-\text{C}(\text{O})\text{O}-\text{CH}=\text{CH}_2$ ) and methyl acrylate ( $\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{O}-\text{CH}_3$ ) are isomers and can be considered as the addition of the  $\text{CH}_3$  and  $\text{CH}_2=\text{CH}$  entities to the ester functionality  $-\text{C}(\text{O})\text{O}-$ , but at different positions. The methyl groups are known to be very unreactive toward Cl atoms in both possible isomer configurations, therefore, the reactivity of the isomers will be governed by the position of the  $\text{CH}_2=\text{CH}$  group. One would expect methyl acrylate to show a lower reactivity toward Cl compared to vinyl acetate since, in the former, the  $-\text{C}(\text{O})-$  will deactivate the double bond toward Cl addition and, in the latter, the O atom will activate the double toward Cl addition as indicated above. A rate coefficient of  $2.14\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K has recently been reported for the reaction of Cl with  $\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{O}-\text{CH}_3$  (Blanco et al. 2008), which is lower than the value of  $2.68\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> determined for the reaction of Cl with vinyl acetate in this work and, thus, is conform with mechanistic expectations.

The value of the rate coefficient determined by Blanco et al. (2008) for the reaction of Cl with methyl acrylate is very similar to the rate coefficients reported for the reactions of Cl with acrolein ( $\text{CH}_2=\text{CHC}(\text{O})\text{H}$ ), methyl vinyl ketone ( $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$ ), and chloromethyl vinyl ketone ( $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_2\text{Cl}$ ) at 298 K, which are listed in Table 2. The values, however, are at odds with a higher rate coefficient reported for the reaction of Cl with acrylic acid ( $\text{CH}_2=\text{CHC}(\text{O})\text{OH}$ ) (Teruel et al. 2007). This aside, at the present state of knowledge, the bulk of the available evidence seems to indicate that both  $-\text{C}(\text{O})\text{R}$  and  $-\text{C}(\text{O})\text{OR}$  groups will have similar influences on the addition of Cl to the attached  $\text{CH}_2=\text{CH}$  group with a rate coefficient of around  $2\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the addition reaction.

A rate coefficient of  $(2.50\pm 0.78)\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> has been measured for the reaction of Cl with butyl acrylate ( $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$ ). If the rate coefficients for reaction at the  $\text{CH}_2=\text{CHC}(\text{O})\text{O}$  and  $-\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$

**Table 2** Room temperature rate coefficients for the reactions of Cl atoms with different organic compounds at atmospheric pressure, except <sup>(a)</sup> performed at low pressure by the discharge flow technique

VOIC	$k_{Cl}/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference
CH <sub>3</sub> C(O)OCH=CH <sub>2</sub>	2.68	This work
CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>3</sub>	0.2	Notario et al. (1998)
	0.137	Cuevas et al. (2005)
CH <sub>2</sub> =CH <sub>2</sub>	0.99	Stutz et al. (1998)
CH <sub>3</sub> CH=CH <sub>2</sub>	2.64	Ezell et al. (2002)
CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	3.38	Ezell et al. (2002)
CH <sub>3</sub> C(O)OCH <sub>2</sub> CH=CH <sub>2</sub>	1.3	This work
CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.776	Notario et al. (1998)
	0.46	Cuevas et al. (2005)
CH <sub>2</sub> =CHCH <sub>2</sub> OH	1.72	Rodriguez et al. (2007)
CH <sub>2</sub> =CHC(O)O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	2.5	This work
CH <sub>3</sub> C(O)O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	1.74	Notario et al. (1998)
	1.23	Cuevas et al. (2005)
CH <sub>2</sub> =CHC(O)H	2.5	Wang et al. (2002)
CH <sub>2</sub> =CHC(O)OH	0.4 <sup>(a)</sup>	Aranda et al. (2003)
	3.99	Teruel et al. (2007)
CH <sub>2</sub> =CHC(O)OCH <sub>3</sub>	2.14	Blanco et al. (2008)
CH <sub>2</sub> =CHC(O)CH <sub>3</sub>	2.0	Wang et al. (2002)
CH <sub>2</sub> =CHC(O)CH <sub>2</sub> Cl	2.0	Wang et al. (2002)

compound entities are additive, one would predict that the rate coefficient for the reaction of Cl with butyl acrylate should be approximately equal to the sum of the rate coefficients for Cl with methyl acrylate and *n*-butyl acetate. As can be seen from the table, there is some uncertainty in the rate coefficient for Cl+*n*-butyl acetate, however taking an average value of  $1.50 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction in combination with a value of  $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for Cl+methyl acrylate would result in a rate coefficient of  $3.50 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of Cl with *n*-butyl acrylate. This estimate is somewhat higher than the value measured in this study and is also outside of the error limit attributed to the measurement. This may just simply be due to the uncertainties in the available rate coefficients for the various compounds or it might imply that the -C(O)OR functional has a greater deactivating effect on an attached CH<sub>2</sub>=CH group than the present data suggests.

As can be seen in Table 2, the reactivities of the unsaturated esters VAC, AAC, and BUAC toward Cl atoms

are considerably higher than those of their corresponding saturated ester analogues. This is a reflection of the different dominating reaction pathways, i.e., the faster Cl addition to the C=C double bond in the unsaturated esters compared to the slower H-atom abstraction for the corresponding, saturated ester analogues. The differing mechanisms will result in considerably different reaction product distributions for unsaturated and saturated esters.

#### 4.3 Atmospheric implications

With respect to the atmospheric implications of the reactions studied, the rate coefficients summarized in Table 1 can be used to calculate the atmospheric lifetimes of the unsaturated esters due to reaction with Cl atoms in comparison to their reactions with the other major atmospheric oxidants OH, NO<sub>3</sub>, and O<sub>3</sub> using the expression:  $\tau_x = 1/k_x[X]$  with X=OH, Cl, NO<sub>3</sub>, or O<sub>3</sub>, where  $k_x$  is the rate coefficient for the reaction of the oxidant X with the ester and [X] is the typical atmospheric concentration of the oxidant. For the calculations, the following oxidant concentrations have been used: [OH]= $2 \times 10^6$  radicals cm<sup>-3</sup> (Hein et al. 1997); [Cl]= $1 \times 10^4$  atoms cm<sup>-3</sup> (Wingenter et al. 1996); [NO<sub>3</sub>]= $5 \times 10^8$  radicals cm<sup>-3</sup> (Shu and Atkinson 1995); and [O<sub>3</sub>]= $7 \times 10^{11}$  molecules cm<sup>-3</sup> (Logan 1985).

The estimated tropospheric lifetimes at room temperature of the esters with the tropospheric oxidants (where data are available) are presented in Table 3. Photolytic loss of the esters will be negligible since they are photolytically stable in the actinic region of the electromagnetic spectrum. The lifetimes indicate that the esters are likely to be removed rapidly in the gas phase, the reaction with OH and NO<sub>3</sub> radicals being the major loss processes for vinyl acetate. Unfortunately, no data are available on the reactions of NO<sub>3</sub> radicals with AAC and BUAC, although, on the basis of structural similarities, it

**Table 3** Estimated tropospheric lifetimes of the unsaturated esters studied in this work with Cl atoms, OH radicals, O<sub>3</sub> molecules, and NO<sub>3</sub> radicals

Unsaturated esters	$\tau_{Cl}$	$\tau_{OH}$	$\tau_{O_3}$	$\tau_{NO_3}$
Vinyl acetate	4 days <sup>a</sup>	3 hours <sup>b</sup>	5 days <sup>c</sup>	4 hours <sup>b</sup>
Allyl acetate	9 days <sup>a</sup>	5 hours <sup>d</sup>	7 days <sup>e</sup>	–
Butyl acrylate	5 days <sup>a</sup>	8 hours <sup>f</sup>	–	–

Rate coefficients used in the calculation of the lifetimes were taken from:

<sup>a</sup> This work

<sup>b</sup> Grosjean and Williams (1992)

<sup>c</sup> Grosjean and Grosjean (1998)

<sup>d</sup> Piquet-Varrault et al. (2002)

<sup>e</sup> Le Calve et al. (2000)

<sup>f</sup> Blanco and Teruel (2008)

is probable that they will show a similar reactivity toward  $\text{NO}_3$  radicals as VAC and thus have a similar lifetime with respect to reaction with this oxidant. Therefore, reactions with both OH and  $\text{NO}_3$  radicals are also likely to be important removal processes for AAC and BUAC.

The short lifetimes for the esters, in the range of a few hours, imply that the unsaturated VOCs are likely to be removed rapidly in the gas phase close to their source of emission with removal by OH radicals dominating. Nevertheless, in coastal areas and in the marine boundary layer, where peak concentrations of Cl atoms as high as  $1 \times 10^5$  atoms  $\text{cm}^{-3}$  can occur (Spicer et al. 1998; Ezell et al. 2002), Cl atom-initiated degradation of vinyl and allyl acetates and butyl acrylate can then be a significant if not dominant homogeneous loss process.

## 5 Conclusions

The kinetics of the reactions of Cl atoms with three  $\alpha,\beta$ -unsaturated esters have been determined for the first time at room temperature and atmospheric pressure. The measured reactivity of these unsaturated and oxygenated VOCs toward Cl atoms is essentially in line with what would be expected from a comparison of the reactivity of structurally similar compounds toward Cl atoms. The kinetic data for the reactions of Cl with the unsaturated esters in combination with other available kinetic data suggests that, while for the reactions of Cl with VAC ( $\text{CH}_3\text{C}(\text{O})\text{OCH}=\text{CH}_2$ ) and AAC ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ ) the addition of Cl to the double bond will dominate, in the case of Cl with BUAC ( $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$ ), both addition of Cl to the double bond and also H-atom abstraction from the *n*-butyl group will be operative.

Although reactions with  $\text{NO}_3$  and mainly OH radicals will determine the atmospheric lifetime of the esters, resulting in short lifetimes in the range of hours and degradation close to their emission sources, since the rate coefficients for the reactions of Cl with the esters are one order of magnitude higher than the corresponding rate coefficients for the reactions with OH radicals, reaction with Cl will be able to compete effectively with the OH reaction in coastal areas where the concentration of Cl can reach a peak value of  $10^5$  atoms  $\text{cm}^{-3}$  at dawn. This would also apply to urban areas where high concentrations of Cl atoms can originate from industrial emissions.

## 6 Recommendations and perspectives

The rate coefficients presented in the present study for the reactions of Cl with three unsaturated esters have only been

performed at room temperature. It would be beneficial to study the reactions over the range of temperatures and pressures typically prevailing in the troposphere. This is also true for the corresponding reactions with OH,  $\text{NO}_3$ , and ozone where in some cases kinetic data is completely missing. In addition, detailed products studies on the Cl reactions would allow (a) the validation and hopefully quantification of the addition and abstraction reaction channels proposed in this study and (b) the construction of complete degradation mechanisms for the reactions. The kinetic and mechanistic data would allow a more realistic representation of the tropospheric chemistry of unsaturated esters in different types of atmospheric models the results of which are used for making atmospheric policy decisions.

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