Gas-phase kinetics of OH radicals reaction with a series of fluorinated acrylates and methacrylates at atmospheric pressure and 298 K

Carmen M. Tovar, Mariano A. Teruel[*]

INFIQC (CONICET, Facultad de Ciencias Químicas-Universidad Nacional de Córdoba), Dpto. de Fisicoquímica. Ciudad Universitaria, 5000 Córdoba, Argentina

HIGHLIGHTS

- First kinetics for a series of OH + fluoro(acrylates and methacrylates).
- Relative rate coefficients by GC-FID detection at 298 K and 1 atm.
- Reactivity trends in terms of F substitutions and hydrocarbon chain length.
- Only fluoromethacrylates reactivity is affected by F substitution.
- Atmospheric lifetimes of hours indicate local impact over air pollution.

GRAPHICAL ABSTRACT
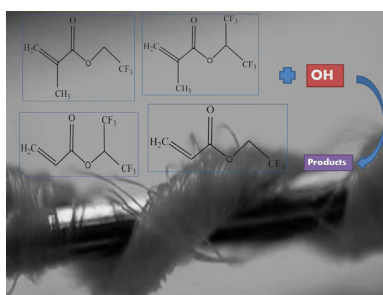
ARTICLE INFO

ABSTRACT

Rate coefficients for the gas phase reactions of OH radicals with 2,2,2-trifluoroethylmethacrylate (k_1) 1,1,1,3,3,3-hexafluoroisopropylacrylate (k_2), 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (k_3), and 2,2,2-trifluoroethylacrylate (k_4) were determined to be $k_1 = (2.54 \pm 0.12) \times 10^{-11}$, $k_2 = (1.41 \pm 0.11) \times 10^{-11}$, $k_3 = (1.65 \pm 0.14) \times 10^{-11}$ and $k_4 = (1.25 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Kinetic experiments were performed at room temperature and atmospheric pressure using the relative-rate technique with GC-FID analysis. This study is the first kinetic for these reactions of OH radicals under atmospheric pressure. Additionally, the rate constants obtained are compared with other halogenated and non halogenated acrylates and methacrylates to develop structure/reactivity relationships in terms of the presence of fluorine and ester groups and the hydrocarbon chain length. The atmospheric implications of the reactions were assessed by the estimation of the tropospheric lifetimes of the title reactions.

1. Introduction

During the past years increased awareness has arisen on a new type of persistent organic pollutants, which contains an alkyl chain typically between 4 and 12 carbon atoms, where all or most of the hydrogen atoms have been replaced by fluorine. This makes the chain very stable and practically non-degradable in the environment. The substances also contain a more reactive functional group or C═C double bond, which may be an alcohol, a carboxylic acid, a sulfonic acid, a phosphoric acid or their derivatives (Jensen et al., 2008). This is the case of the fluorinated acrylates and methacrylates, which besides presenting halogenated groups possess highly reactive olefinic carbons.

The unsaturated oxygenates are continually introduced into the atmosphere and the kinetics and degradation pathways under atmospheric conditions of many of these compounds are still largely unknown (Mellouki et al., 2003; Calvert et al., 2011).

* Corresponding author.
 E-mail address: mteruel@fcq.unc.edu.ar (M.A. Teruel).

Unsaturated esters are employed in the extraction of chemicals, as intermediates in the manufacture of polymers and in the manufacture of circuit boards (Barnes, 2010).

Fluorinated acrylates and methacrylates are unsaturated esters with a wide range of industrial applications, since they are functional monomers used for the development of a new family of fluorine-containing vinyl polymers for Hi-Tech applications. These vinyl polymers generally possess a unique combination of the thermal and chemical stability, lack of solubility and high hydrophobicity and oleophobicity. For example a polyacrylate containing 2,2,2-trifluoroethylmethacrylate units has been used as photocross linkable material because of their good surface properties for coatings, and the poly (TFEM-co-BE) copolymers (where BE stands for butyl vinyl ether) is used in stone protecting coatings for the preservation of monuments, especially in Italy due to their photochemical stability, property that is improved by the presence of the trifluoromethyl group preventing from cyclization reactions (Boschet et al., 2010).

On the other hand, fluorine containing polymers have unique properties like excellent resistance to heat, chemicals, flame, fuels and oils. Furthermore, they show low surface tension, low friction coefficient and high optical clarity. Fluoroelastomers have several important applications *e.g.* in O-rings, gaskets and in different automobile parts which requires high temperature oil resistance property (Koiry et al., 2013).

The atmospheric degradation of unsaturated oxygenated compounds will be initiated mainly by chemical reaction with OH and NO_3 radicals and O_3 molecules contributing to tropospheric ozone production and the formation of the other secondary photo-oxidants in polluted areas. That is the case of the formation of oxygenated intermediate volatility organic compounds which could potentially produce secondary organic aerosols (SOA).

The aim of this work thus, was to investigate the kinetics of the reaction of OH radicals with 2,2,2-trifluoroethylmethacrylate (TFEM), 1,1,1,3,3,3-hexafluoroisopropylacrylate (HXIA), 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HXIM) and 2,2,2-trifluoroethylacrylate (TEA) at 298 K and at 760 Torr of air:
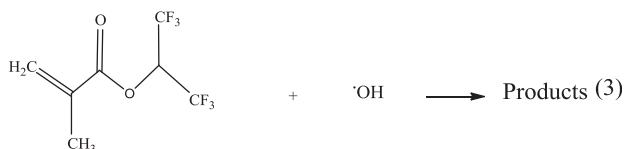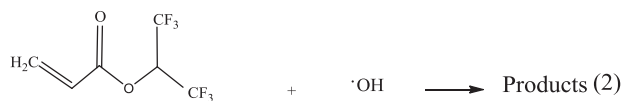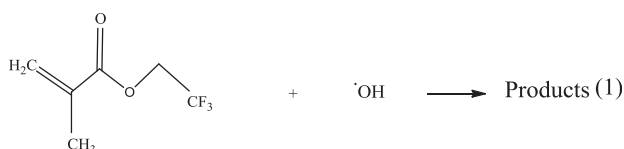
Only a limited number of kinetic studies have been performed for the reaction of OH radicals with hydrogenated unsaturated esters (Le Calve et al., 2000; Teruel et al., 2006, 2012; Blanco et al., 2006, 2009; Blanco and Teruel, 2008, 2011; Colomer et al., 2013) and only one study has been reported for the OH initiated oxidation of an unsaturated fluorinated ester (CH_2=$CHC(O)O(CH_2)_2C_4F_9$) performed in a 140 L Pyrex reactor coupled with FTIR detection (Butt et al., 2009).

To the best of our knowledge no previous kinetic results were reported in literature. Thus, this work provides the first kinetic study for the reaction of OH with 2,2,2-trifluoroethylmethacrylate; 1,1,1,3,3,3-hexafluoroisopropylacrylate; 1,1,1,3,3,3-hexafluoroisopropylmethacrylate and 2,2,2-trifluoroethylacrylate.

The present results are compared with similar compounds varying the position and the nature of the deactivating groups with respect to the ester functional group and the length of the hydrocarbon chain.

Atmospheric lifetimes of the VOCs studied in this work, by their reactions with OH radicals, were calculated taking into account the experimental rate constants obtained.

2. Experimental section

The experimental set-up consisted of an 80 L colapsile Teflon bag located in a wooden box with the internal walls covered with aluminium foil operated at (760 ± 10) Torr and (298 ± 1) K. Measured amounts of the organic reactants were flushed from calibrated bulbs into the reaction chamber with a stream of ultra-pure nitrogen. The bag was then filled to its full capacity at atmospheric pressure with ultra-pure nitrogen. H_2O_2 was used to generate OH radicals by its photolysis using a set of germicidal lamps:

$$H_2O_2 + h\nu(\lambda \sim 254 \text{ nm}) \rightarrow 2OH \tag{5}$$

These lamps provide UV-radiation with a λ maximum around 254 nm. In the present work, typically six of these lamps were used to produce OH radicals. Reaction mixtures consist of a reference organic compound and the sample organic reactant diluted in nitrogen. The mixtures were photolysed for a period of 2–5 min, in steps of 10 min, and after each photolysis step, the decrease in the concentration of the reactant was determined. Periodically, gas samples were removed from the Teflon bag, to monitor the reactant concentrations, using calibrated gas Hamilton gas tight. The organics were followed by a gas chromatograph (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held from 180 to 200 °C for all compounds and the temperature of the injector and detector system was 200 °C and 300 °C, respectively.

Before each set of experiments the bag was cleaned by filling in with a mixture of O_2 and N_2 which was irradiated for 15–25 min, to produce O_3. After this procedure, the bag was cleaned again by repeated flushing with N_2 and checked before performing the experiments by gas chromatography that were no observable impurities.

In the presence of the oxidant OH radical the fluorinated acrylates and methacrylates (FAM) studied and the reference decay through the following reactions:

$$\cdot OH + FAM \rightarrow Products \tag{6}$$

$$\cdot OH + Reference \rightarrow Products \tag{7}$$

Provided that the reference compound and the reactant are lost only by reactions (6) and (7), it can be shown that:

$$\ln\left\{\frac{[FAM]_0}{[FAM]_t}\right\} = \frac{k_{FAM}}{k_{ref}}\ln\left\{\frac{[Ref]_0}{[Ref]_t}\right\} \tag{I}$$

where $[FAM]_0$, $[Ref]_0$, $[FAM]_t$, $[Ref]_t$, are the concentrations of the fluorinated acrylates and methacrylates and the reference compound at times $t = 0$ and t, respectively and k_{FAM} and k_{ref} are the rate constants of the reactions (6) and (7) respectively.

The relative rate technique relies on the assumption that the fluorinated compounds and the reference compounds are removed solely by reaction with OH radicals. To verify this assumption, mixtures of hydrogen peroxide and air with the fluorinated methacrylate or acrylate and the reference compound were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the precursor of OH (hydrogen peroxide), in the absence of UV light, was of negligible importance over the typical time periods used in this work.

Furthermore, to test for possible photolysis of the reactants used, mixtures of the fluorinated acrylates and methacrylates in air, in the absence of hydrogen peroxide, were irradiated for 30 min using the output of all the germicidal lamps surrounding the chamber. No significant photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 247–494 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) for the fluorinated acrylates and methacrylates, and 329–658 ppm for diethylether, 3-chloropropene and 2-methyl-3-buten-2-ol used as reference compounds.
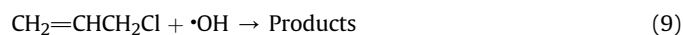
3. Materials

The following chemicals with purities as stated by the supplier were used without further purification: nitrogen (AGA, 99.999%), oxygen (AGA, 99.999%), 2,2,2-trifluoroethylmethacrylate (Aldrich, 99%); 1,1,1,3,3,3-hexafluoroisopropylacrylate; 2,2,2-trifluoroethylacrylate (Aldrich, 99%); 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (Aldrich, 99%) diethylether (Fluka, 99%), 3-chloropropene (Fluka, 98%) and 2-methyl-3-buten-2-ol (Aldrich, 96%) and H$_2$O$_2$ (Cicarelli, 60% wt).

4. Results

Relative rate coefficients for the reactions of OH radicals 2,2,2-trifluoroethylmethacrylate; 1,1,1,3,3,3-hexafluoroisopropylacrylate; 1,1,1,3,3,3-hexafluoroisopropylmethacrylate and 2,2,2-trifluoroethylacrylate were determined by comparing the OH reaction of the fluorinated acrylates and methacrylates with the reference compounds from Eq. (I). A straight line was fitted to the data by the linear least-squares procedure. The losses of unsaturated and fluorinated esters studied by its reactions with OH radicals are shown using different reference compounds in Fig. 1.

The OH radical rate coefficients for each of the fluorinated acrylates and methacrylates were measured relative to different reference compounds:

$$(CH_3CH_2)_2O + {}^\bullet OH \rightarrow Products \tag{8}$$

$$CH_2{=}CHCH_2Cl + {}^\bullet OH \rightarrow Products \tag{9}$$

$$CH_2{=}CHC(CH_3)_2OH + {}^\bullet OH \rightarrow Products \tag{10}$$

The following values of the reference rate coefficients (in units of cm^3 molecule^{-1} s^{-1}) were used to place the rate coefficients for the reactions of the FAM with OH radicals on an absolute basis: $k_8 = (1.36 \pm 0.11) \times 10^{-11}$ (Mellouki et al., 1995),

$k_9 = (1.69 \pm 0.07) \times 10^{-11}$ (Albaladejo et al., 2003), $k_{10} = (5.67 \pm 0.13) \times 10^{-11}$ (Papagni et al., 2001).

Table 1 shows the data on relative rate coefficients k_{FAM}/k_{Ref} and absolute rate coefficients k_{FAM} at room temperature (298 K). The ratios were obtained from the average of four experiments using different initial concentrations of the fluorinated acrylates and methacrylates. The rate coefficients obtained by averaging the values from different experiments were the following:

$$k_1 = (2.54 \pm 0.12) \times 10^{-11} cm^3\ molecule^{-1}\ s^{-1}$$

$$k_2 = (1.41 \pm 0.11) \times 10^{-11} cm^3\ molecule^{-1}\ s^{-1}$$

$$k_3 = (1.65 \pm 0.14) \times 10^{-11} cm^3\ molecule^{-1}\ s^{-1}$$

$$k_4 = (1.25 \pm 0.13) \times 10^{-11} cm^3\ molecule^{-1}\ s^{-1}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have also considered the corresponding error on the reference rate coefficients (8–10).

5. Discussion

Although there have been no previous studies of k_1, k_2, k_3, k_4, we can compare our results with the reactions of the corresponding hydrogenated acrylates and methacrylates. In Table 2 are tabulated room temperature rate coefficients of hydrogenated and halogenated unsaturated esters from this work and previous results.

From Table 2 it is possible to observe a decrease in the reaction rate coefficients for the compounds when H atoms are replaced by fluorine atoms, $k_{CH_2=C(CH_3)C(O)OCH_2CH_3} = 4.58 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH_2=C(CH_3)C(O)OCH_2CF_3} = 2.54 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{CH_2=CHC(O)OCH_2CH_3} = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH_2=CHC(O)OCH_2CF_3} = 1.25 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This trend can be explained by the negative inductive effect of F atoms attached to the olefinic carbons together with the possibility of the hydrogen bonds, that are formed between atoms of F and OH radicals, prevent rapid addition to the double bond. Hydrogen bonds, formed between the OH radical and fluorine atoms, would increases in importance with fluorine substitution, an effect already observed in fluorinated alkenes (Hurley et al., 2007; Søndergaard et al., 2007).

For methacrylate esters it can be shown a decrease in the reaction rate coefficients with de degree of florination: $k_{CH_2=C(CH_3)C(O)OCH_2CF_3} = 2.54 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH_2=C(CH_3)C(O)OCH_2(CF_3)_2} = 1.65 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This trend could be due to the electron withdrawing effect of F atoms, leading to a decrease in the rate coefficient value.

On the other hand, for acrylate esters, there is not a significant change in the reaction rate coefficient with the number of fluorine atoms substituents: $k_{CH_2=CHC(O)OCH_2CF_3} = 1.25 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} < $k_{CH_2=CHC(O)OCH_2(CF_3)_2} = 1.41 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Additionally, structure activity relationships (SAR), using the 'Environmental Protection Agency' rate constant calculation software, AOPWIN v1.91 (US Environmental Protection Agency, 2000) based on the SAR method developed by Kwok and Atkinson, 1995, were used to calculate the rate coefficients for the reactions of OH with the FAM studied. Rate constant values for the reactions of OH radicals with 2,2,2-trifluoroethylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylacrylate and 2,2,2-trifluoroethylacrylate, were determined to be (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}): 1.82, 1.81, 0.92, 0.93,
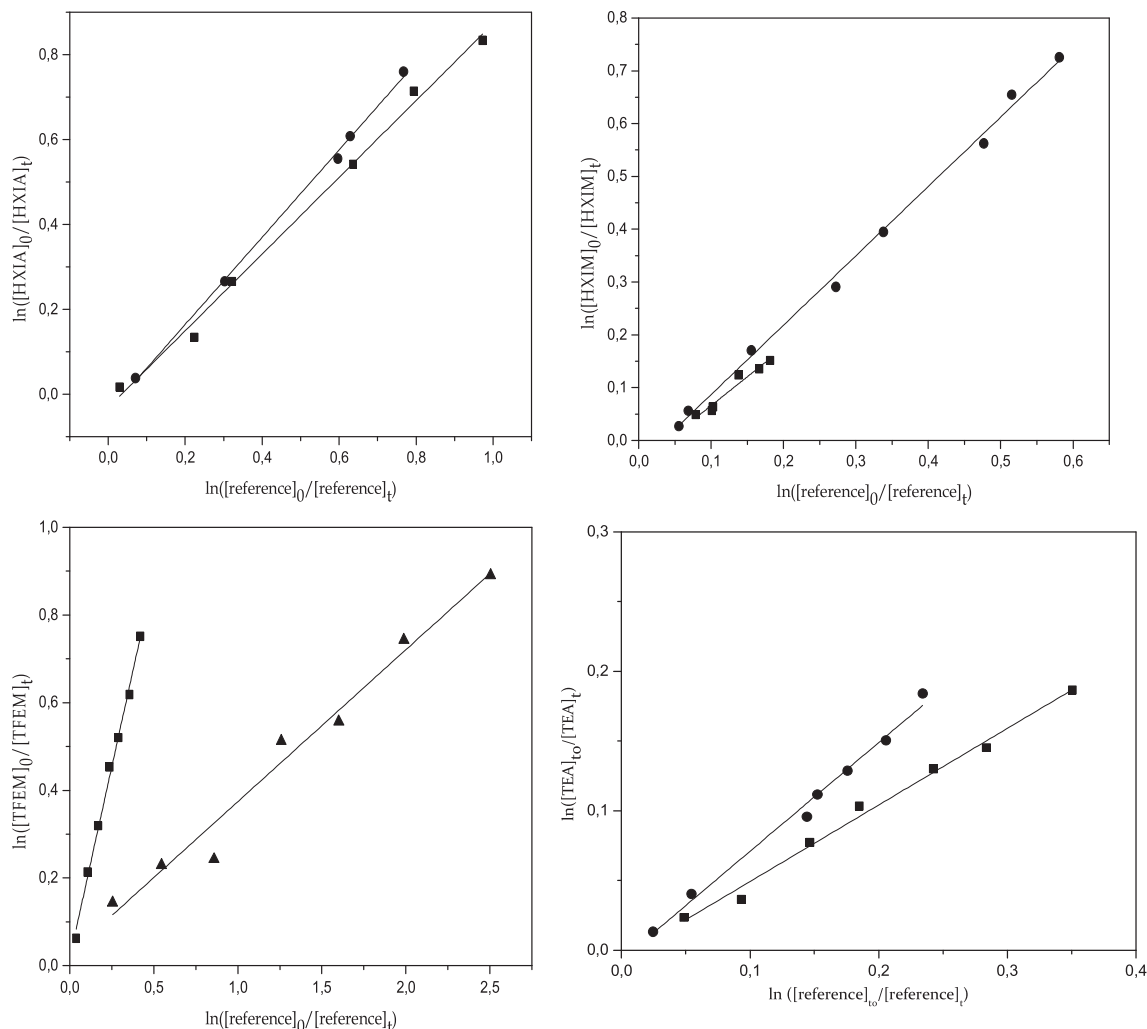
Fig. 1. Exemplary plots of the kinetic data for the reactions of OH radical with 1,1,1,3,3,3-hexafluoroisopropylacrylate, 1,1,1,3,3,3-hexafluoroisopropylmethacrylate,2,2,2-trifluoroethylacrylate, and 2,2,2-trifluoroethylmethacrylatemeasured relative to the same reactions with the reference compounds: diethylether (●), 3-chloropropene (■) and 2-methyl-3-buten-2-ol (▲) in nitrogen at room temperature and atmospheric pressure.

Table 1

Slopes k_{FAM}/k_{ref} and the obtained rate coefficients for the reaction of OH with 2,2,2-trifluoroethylmethacrylate (TFEM), 1,1,1,3,3,3-hexafluoroisopropylacrylate (HXIA), 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HXIM), and 2,2,2-trifluoroethylacrylate (TEA), and at 298 K in 760 Torr of nitrogen.

FAM	Reference	k_{FAM}/k_{ref}	k_{FAM} (cm^3 molecule^{-1} s^{-1})
TFEM	3-Chloropropene	(1.74 ± 0.02)	$(2.95 \pm 0.12) \times 10^{-11}$
	3-Chloropropene	(1.58 ± 0.06)	$(2.67 \pm 0.11) \times 10^{-11}$
	2-Methyl-3-buten-2-ol	(0.46 ± 0.05)	$(2.58 \pm 0.06) \times 10^{-11}$
	2-Methyl-3-buten-2-ol	(0.35 ± 0.02)	$(1.97 \pm 0.05) \times 10^{-11}$
	Average		$(2.54 \pm 0.12) \times 10^{-11}$
HXIA	Diethylether	(0.96 ± 0.01)	$(1.31 \pm 0.11) \times 10^{-11}$
	Diethylether	(1.03 ± 0.02)	$(1.39 \pm 0.11) \times 10^{-11}$
	3-Chloropropene	(0.90 ± 0.03)	$(1.53 \pm 0.06) \times 10^{-11}$
	3-Chloropropene	(0.84 ± 0.03)	$(1.41 \pm 0.06) \times 10^{-11}$
	Average		$(1.41 \pm 0.11) \times 10^{-11}$
HXIM	Diethylether	(1.07 ± 0.02)	$(1.44 \pm 0.12) \times 10^{-11}$
	Diethylether	(1.31 ± 0.03)	$(1.78 \pm 0.14) \times 10^{-11}$
	3-Chloropropene	(0.92 ± 0.02)	$(1.55 \pm 0.06) \times 10^{-11}$
	3-Chloropropene	(1.09 ± 0.12)	$(1.84 \pm 0.08) \times 10^{-11}$
	Average		$(1.65 \pm 0.14) \times 10^{-11}$
TEA	Diethylether	(0.76 ± 0.03)	$(1.04 \pm 0.08) \times 10^{-11}$
	Diethylether	(1.20 ± 0.06)	$(1.61 \pm 0.13) \times 10^{-11}$
	3-Chloropropene	(0.84 ± 0.01)	$(1.41 \pm 0.05) \times 10^{-11}$
	3-Chloropropene	(0.55 ± 0.02)	$(0.93 \pm 0.04) \times 10^{-11}$
	Average		$(1.25 \pm 0.13) \times 10^{-11}$

respectively. Table 3 shows the rate coefficients values obtained by SAR calculations and those obtained experimentally from this work and from literature. It can be seen that the calculated rate coefficients are very close, within the experimental errors, with the rate coefficient values obtained in this work of (2.54 ± 0.12), (1.65 ± 0.14), (1.41 ± 0.11), $(1.25 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.

Table 2

Comparison of the rate coefficients values for the reaction of OH radicals with hydrogenated esters and fluorinated acrylates and methacrylates at 298 K.

Unsaturated ester	$k_{OH(298 \ K)}$ (cm^3 molecule^{-1} s^{-1})	Reference
CH$_2$=C(CH$_3$)C(O)OCH$_3$	$(4.15 \pm 0.32) \times 10^{-11}$	Blanco et al., 2006
CH$_2$=C(CH$_3$)C(O)OCH$_2$CH$_3$	$(4.58 \pm 0.59) \times 10^{-11}$	Blanco et al., 2006
CH$_2$=C(CH$_3$)C(O)O(CH$_2$)$_3$CH$_3$	$(7.08 \pm 0.75) \times 10^{-11}$	Blanco et al., 2006
CH$_2$=C(CH$_3$)C(O)O CH(CF$_3$)$_2$	$(1.65 \pm 0.14) \times 10^{-11}$	This work
CH$_2$=C(CH$_3$)C(O)OCH$_2$CF$_3$	$(2.54 \pm 0.12) \times 10^{-11}$	This work
CH$_2$=CHC(O)OCH$_3$	$(1.3 \pm 0.2) \times 10^{-11}$	Teruel et al., 2006
CH$_2$=CHC(O)OCH$_2$CH$_3$	$(1.7 \pm 0.4) \times 10^{-11}$	Teruel et al., 2006
CH$_2$=CHC(O)O(CH$_2$)$_2$CH$_3$	$(1.80 \pm 0.26) \times 10^{-11}$	Blanco et al., 2008
CH$_2$=CHC(O)OCH(CF$_3$)$_2$	$(1.41 \pm 0.11) \times 10^{-11}$	This work
CH$_2$=CHC(O)OCH$_2$CF$_3$	$(1.25 \pm 0.13) \times 10^{-11}$	This work
CH$_2$=CHC(O)O(CH$_2$)$_2$C$_4$F$_9$	$(1.13 \pm 0.12) \times 10^{-11}$	Butt et al., 2009.

Table 3
Comparison of the experimental (k_{exp}) from this work and calculated by US EPA AOPWIN (k_{calc}) room-temperature rate coefficients for fluorinated acrylates and methacrylates.

Unsaturated ester	k_{calc} (cm³ molecule⁻¹ s⁻¹)	k_{exp} (cm³ molecule⁻¹ s⁻¹)
$CH_2=C(CH_3)C(O)OCH_2CF_3$	1.82×10^{-11}	$(2.54 \pm 0.12) \times 10^{-11}$
$CH_2=C(CH_3)C(O)O\ CH(CF_3)_2$	1.81×10^{-11}	$(1.65 \pm 0.14) \times 10^{-11}$
$CH_2=CHC(O)OCH(CF_3)_2$	0.92×10^{-11}	$(1.41 \pm 0.11) \times 10^{-11}$
$CH_2=CHC(O)OCH_2CF_3$	0.93×10^{-11}	$(1.25 \pm 0.13) \times 10^{-11}$
$CH_2=CHC(O)OCH(CH_3)_2$	1.26×10^{-11}	–
$CH_2=C(CH_3)C(O)O\ CH(CH_3)_2$	2.15×10^{-11}	–

In order to check the contribution of the H- abstraction to the overall rate coefficients, SAR calculation using the US EPA AOPWIN program were performed giving the results of $k_{H-abstraction}$(in units of 10^{-12} cm³ molecule⁻¹ s⁻¹) of: 0.24, 0.0156, 0.15 and 0.1061 for the reactions of OH with 2,2,2-trifluoroethylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylacrylate and 2,2,2-trifluoroethylacrylate, respectively.

Rate coefficient values for those non halogenated compounds that no have previous experimental determinations ($CH_2=C(CH_3)C(O)OCH(CH_3)_2$ and $CH_2=CHC(O)OCH(CH_3)_2$) were calculated to be (in units of 10^{-11} cm³ molecule⁻¹ s⁻¹): 2.15 and 1.25, respectively. These values were used to determine the ratio between the rate coefficients between halogenated and non halogenated acrylates and methacrylates. The calculations were performed using software, AOPWIN v1.91 (US Environmental Protection Agency, 2000). Table 4 shows the ratio of the rate coefficients of hydrogenated methacrylates and acrylates and the corresponding halogenated methacrylates and acrylates (MH/MF-AH/AF) studied in this work. The ratios obtained, for acrylates and methacrylates, are quite similar taking into account the experimental error and the use of calculated rate coefficients, giving extra confidence to the results obtained in the present work.

5.1. Atmospheric implications

Atmospheric lifetimes τ_{OH}, of the esters studied in this work were estimated through the expression $\tau_x = 1/k_x\ [x]$, with X = OH and where k_x is the rate coefficient for the reaction of the oxidant OH with the halogenated acrylates and methacrylates and [X] is the typical atmospheric concentration of the OH radical:

FAM	k_{OH} (cm³ molecule⁻¹ s⁻¹)	τ_{OH} (hours)
HXIA	1.41×10^{-11}	10
HXIM	1.65×10^{-11}	8
TEA	1.25×10^{-11}	11
TFEM	2.54×10^{-11}	5

The rate coefficients (k_{OH}) were taken from this work and typical atmospheric concentrations were used, a 12 h average concentration of OH [OH] $= 2 \times 10^6$ molecule⁻¹ cm³ (Hein et al., 1997).

Unfortunately, no kinetic data are available for the reactions for HXIA, HXIM, TFEM, TEA with O_3 molecules as well as other tropospheric oxidants like NO_3 radical or Cl atoms. However, the available kinetic data shows that the reaction with OH radicals is the dominant degradation process of unsaturated esters in the atmosphere with lifetimes of a few hours (Blanco et al., 2006, 2009; Teruel et al., 2006), it could be expected that the main sink of these fluorinated compounds will be reaction with OH radicals.

Loss of these compounds by photolysis can be considered negligible, since they are photolytically stable in the actinic region of the electromagnetic spectrum and the concentration of the esters did not show any variation when were irradiated in the absence of OH precursor before the kinetic experiments.

2,2,2-trifluoroethylmethacrylate; 1,1,3,3,3-hexafluoroisopropylacrylate; 1,1,1,3,3,3-hexafluoroisopropylmethacrylate and 2,2,2-trifluoroethylacrylate have lifetimes in the range of 5–11 h which indicate that these compounds will be degraded close to their emission sources. Consequently, the fate of the products arising from the OH-initiated oxidation of the VOCs studied will be important since the atmospheric oxidation of these products can also contribute to ozone, long-lived nitrogen containing compounds and other oxidants in the troposphere.

The halogenated products of these compounds, mostly halogenated glyoxylates and pyruvates, may further react with the OH radical to give fluorinated aldehydes that could contribute to the formation of ozone and secondary organic aerosols (SOA). The interactions with the last occurs in the gas phase as well in the particle phase, and it is known from previous studies that halogens take part in the ageing process of organic aerosols (Kroll et al., 2011).

Furthermore, fluorinated carboxylic acids are expected to be generated by the oxidation of fluoro glyoxylates and pyruvates to be potential pollutants which could be transported over long distances leading stronger acids than their nonfluorinated counterparts that could affect seriously the biosphere as it is shown in the following exemplary mechanism of OH-initiated degradation of 2,2,2-Trifluoroethylacrylate (TEA) in the presence of NOx:

Table 4
Room temperature rate coefficients ratios between fluorinated acrylates and methacrylates with respect to the corresponding hydrogenated esters.

Methacrylates	$k_{MH/MF}$	Acrylates	$k_{AH/AF}$
$CH_2=C(CH_3)C(O)OCH_2CH_3/CH_2=C(CH_3)C(O)OCH_2CF_3$	1.73	$CH_2=CHC(O)OCH_2CH_3/CH_2=CHC(O)OCH_2CF_3$	1.83
$CH_2=C(CH_3)C(O)OCH(CH_3)_2/CH_2=C(CH_3)C(O)O\ CH(CF_3)_2$	1.30	$CH_2=CHC(O)OCH(CH_3)_2/CH_2=CHC(O)OCH(CF_3)_2$	0.89
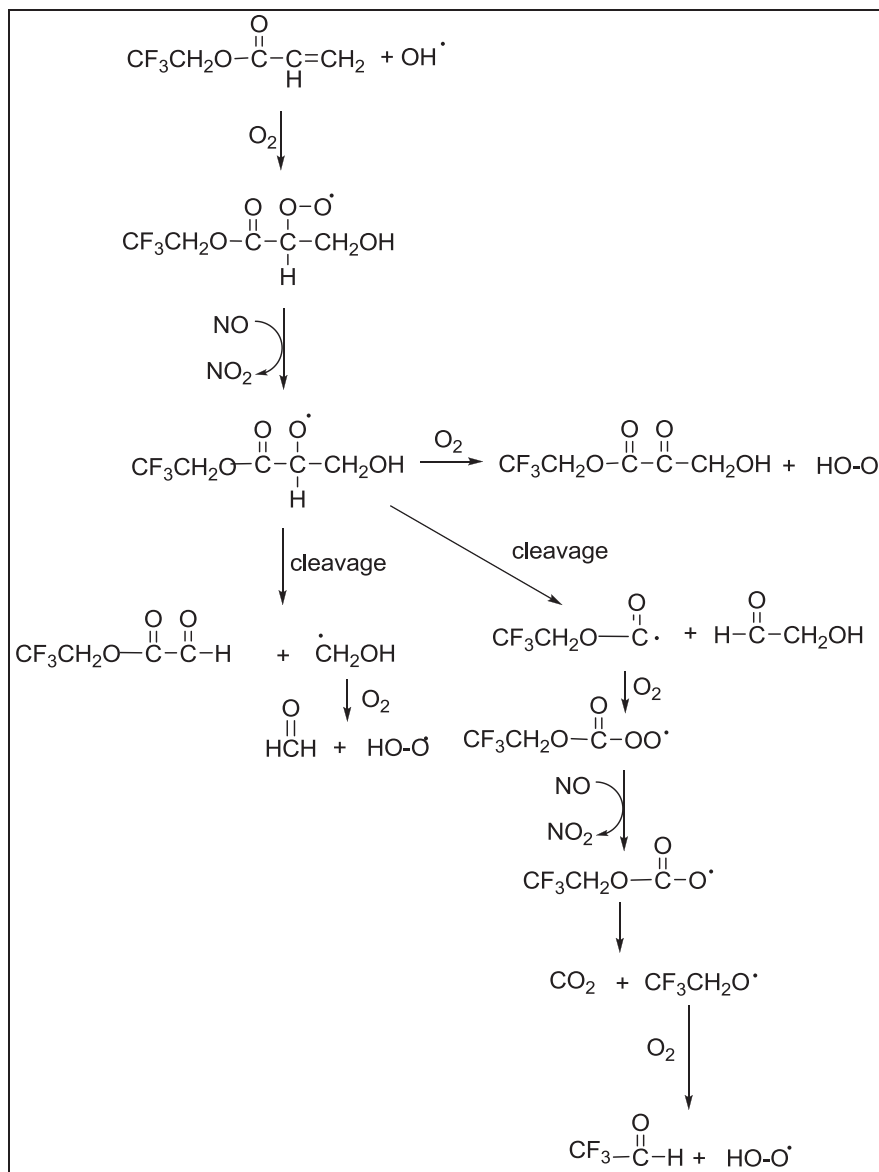
Acknowledgements

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