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Atmospheric degradation of industrial fluorinated acrylates and

methacrylates with Cl atoms at atmospheric pressure and 298 K

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Abstract

The gas-phase reaction of Cl atom with 2,2,2-trifluoroethylacrylate (k_1), 1,1,1,3,3,3-hexafluoroisopropylacrylate (k_2), 2,2,2-trifluoroethylmethacrylate (k_3) and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (k_4), have been investigated at 298 K and 1 atm using the relative method by gas chromatography coupled with flame ionization detection (GC-FID). The values obtained are (in cm^3 molecule^{-1} s^{-1}): k_1(Cl+CH$_2$=CHC(O)OCH$_2$CF$_3$) = (2.41±0.57) ×10^{-10}, k_2(Cl+CH$_2$=CHC(O)OCH(CF$_3$)$_2$) = (1.39±0.34) ×10^{-10}, k_3(Cl+CH$_2$=C(CH$_3$)C(O)OCH$_2$CF$_3$) = (2.22±0.45) ×10^{-10}, and k_4(Cl +CH$_2$=C(CH$_3$)C(O)OCH(CF$_3$)$_2$ = (2.44±0.52) × 10^{-10}. Products identification studies were performed by solid-phase microextraction (SPME) method, with on-fiber products derivatization using o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride, coupled with gas chromatography with mass spectrometry detection (GC-MS). Chloroacetone, trifluoroacetaldehyde and formaldehyde were observed as degradation products and a general mechanism is proposed. Additionally, reactivity trends and atmospheric implications are discussed. Significant ozone photochemical potentials (POCP) and acidification potentials lead to local and or regional impact of the esters under study although is expected to a have a minor impact on global warming and climate change.

1. Introduction

Atmospheric chemistry is currently focused on a number of major environmental issues. Halogenated species, as unsaturated halogenated esters, has attracted a great deal of research interest with implications to gas phase interactions in the troposphere. They present an important chemistry since are widely emitted into the atmosphere from high industrial production, processing and disposal (Takagi et al., 1997; Lu et al., 2013; Zhao et al., 2013; Girard et al., 2014). The large-scale production is due to its many applications, among them we can mention: chemical extraction, manufacture of polymers, precursors in cosmetic aromatic bases, cleaning agents and components of electronics, which could result in release of these compounds into the atmosphere (Barnes, 2010). According to the oxygenated functionalities in the compound, many unsaturated OVOCs will be as reactive and sometimes more reactive than their analogous alkenes, also the double bond of the molecule is very receptive to the addition of oxidants such as tropospheric OH, NO_3 radicals, and O_3 molecules. Reactions with Cl atoms play an important role in atmospheric chemistry since VOCs react with them generally in an order of magnitude faster than OH reactions.

It has been observed that on costal urban areas, for brief period of time at sunrise the Cl concentration produced by photolysis of molecular chlorine (Cl_2) can be 1×10^5 atoms cm^{-3} or higher in the marine boundary layer (Spicer et al., 1998; Lawler et al., 2009). Furthermore, it has been detected significant levels of photolabile nitrile chloride ($ClNO_2$) species in mid continental areas, all of this has expanded the knowledge about the atmospheric degradation of VOCs with Cl atoms chemistry (Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011, Philips et al., 2012). Unsaturated halogenated in these work contain Fluorine (F) atom and it is known that fluorine atom is the most electronegative of the elements its replacement by a hydrogen atom. The substitution of a hydrogen atom for a fluorine atom in an organic molecule modifies its thermal, chemical and biological characteristics. The bond formed by

78   C-F atoms is very strong, but the intramolecular interactions of the fluorocarbons are weak.

79   As a result, a unique combination of fluorocarbon properties, such as chemical, thermal and

80   biological inertia, low solubility in water and polar and non-polar organic solvents, high

81   density, flow ability, compressibility and high dielectric constants are obtained (Johns and

82   Stead, 2000). The widespread use of these fluoropolymers could have a great impact on the

83   quality of the air and consequently on the environmental ones, among them we can mention

84   the climatic change (McCulloch, 2003). The unsaturated halogenated esters acrylates and

85   methacrylates have many industrial applications, since they have, monomers used for develop

86   a family of fluorinated compounds that contain vinyl polymers for Hi-Tech applications

87   (Boschet et al., 2010). Furthermore, fluorine containing polymers (fluoroelastomers) have

88   several important applications e.g. in O-rings, gaskets and in different automobile parts which

89   requires high temperature oil resistance property (Koiry et al., 2013). Halogenated acrylates

90   and methacrylates are listed as a high (H) production (P) volume (V) chemicals in the OECD

91   (Organisation for Economic Co-operation and Development) integrated HPV database

92   (http://cs3-hq.oecd.org/scripts/hpv/index.asp).   We have previously reported the rate

93   coefficients of fluorinated acrylates and methacrylates 2,2,2-trifluoroethylacrylate,

94   1,1,1,3,3,3-hexafluoroisopropylacrylate, 2,2,2-trifluoroethylmethacrylate and 1,1,1,3,3,3-

95   hexafluoroisopropylmethacrylate initiated by OH radicals using relative method by GC-FID

96   (Tovar and Teruel, 2014). In order to increase the knowledge of unsaturated fluoresters, it is

97   necessary to assess the importance of other sink of these industrial fluorinated compounds as

98   the gas-phase reaction of the unsaturated halogenated acrylates and methacrylates together

99   with to study the products obtained to postulate atmospheric chemical mechanisms for Cl

100   atoms reactions. Due to the importance of Cl-initiated degradation reactions and the absence

101   of kinetic and product data, in this work, we present for the first time rate coefficients

102   determinations of the reactions of 2,2,2-trifluoroethylacrylate (TFEA), 1,1,1,3,3,3-

103　hexafluoroisopropylacrylate (HFIA), 2,2,2-trifluoroethylmethacrylate (TFEM) and

104　1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HFIM) with Cl atoms at 298 K and 760 Torr:

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106　　　　　　　　$Cl + CH_2=CHC(O)OCH_2CF_3$　　　　$\rightarrow$ Products　　(1)

107　　　　　　　　$Cl + CH_2=CHC(O)OCH(CF_3)_2$　　$\rightarrow$ Products　　(2)

108　　　　　　　　$Cl + CH_2=C(CH_3) C(O)OCH_2CF_3 \rightarrow$ Products　　(3)

109　　　　　　　　$Cl + CH_2=C(CH_3) C(O)OCH(CF_3)_2 \rightarrow$ Products　　(4)

110　To the best of our knowledge, the rate coefficients for the reactions of Cl atoms with the

111　halogenated unsaturated esters have not been previously reported. Hence, the kinetic data

112　presented are the first determinations of the title reactions. Kinetic results are rationalized in

113　terms of reactivity trends by comparison with others unsaturated halogenated esters. In

114　addition, product studies using the GC-MS technique under atmospheric conditions were

115　carried out for the (1-4) reactions and the degradation pathways in the atmosphere are

116　discussed. Chloroacetone and formaldehyde were identified as the main products of reaction

117　of methacrylates with Cl atoms. In regard to the reaction of 2,2,2-trifluoroacrylate with Cl

118　atoms, formaldehyde and trifluoroacetaldeyde were identified as the main products of

119　reaction, whereas that, in the reaction between 1,1,1,3,3,3-hexafluoroisopropilacrylate with

120　Cl atoms, formaldehyde it has been identified, as unike product of this reaction.

121　To assess the possible atmospheric implications of the studied reactions, atmospheric

122　lifetimes of the fluorinated and unsaturated esters involved were calculated taking into

123　account the experimental rate coefficients obtained in this work. Environmental impact is

124　discussed at local, regional and global scale by the determination of ozone photochemical

125　potential (POCP), acidification potential and global warming potential of the unsaturated

126　esters studied in the present work.

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2. Experimental

The kinetic experiments were performed in a Teflon chamber of 80-liter placed in a wooden box with the internal walls covered with aluminum foil. Organic reactants were measured from calibrated bulbs and were introduced into the chamber through a stream of nitrogen. Then, the chamber was filled to its full capacity at atmospheric pressure with nitrogen. We have used nitogen as bath gas for the kinetics experiments and synthetic air for the products distribution analysis.

Cl atoms were generated by photolysis at 254 nm of $ClC(O)C(O)Cl$:

$$ClC(O)C(O)Cl + h\nu \rightarrow 2Cl + 2CO \qquad (5)$$
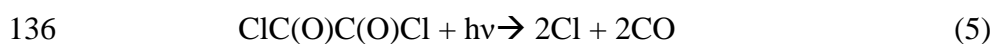
Before each experiment, the reactor was cleaned by filling it with a mixture of O_2 and N_2 which was photolyzed for 10 min using 6 germicidal lamps (Philips 30W) with a UV emission at 254 nm, to produce O_3. After this procedure, the reactor was cleaned again by repeated flushing with N_2 and checked before performing the experiments by gas chromatography that there were no observable impurities. Gas samples were taken from the Teflon reactor using calibrated gas syringes. The organic compounds were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held at a temperature of 160 ºC for these compounds.

In the presence of Cl atom, halogenated unsaturated esters (HUE) 2,2,2-trifluoroethylacrylate(TFEA), 1,1,1,3,3,3-hexafluoroisopropylacrylate (HFIA), 2,2,2-trifluoroethylmethacrylate (TFEM), 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HFIM) and the reference compounds, decay through the following reactions:

$$Cl + HUE \qquad \rightarrow \quad Products \qquad (6)$$

$$Cl + Reference \qquad \rightarrow \quad Products \qquad (7)$$

151   Provided that the reference compound and the reactant are lost only by reactions (6) and (7),

152   then it can be shown that:

153
$$\ln\left\{\frac{[\text{HUE}]_0}{[\text{HUE}]_t}\right\} = \frac{k_{HUE}}{k_{\text{Re}f}}\ln\left\{\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right\} \qquad (8)$$

154   where, [Fluorinated ester]$_0$, [Reference]$_0$, [Fluorinated ester]$_t$ and [Reference]$_t$ are the

155   concentrations of the halogenated esters and references compounds at times $t=0$ and t, k_6 and

156   k_7 are the rate coefficients of reactions (6) and (7), respectively.

157   The relative rate technique relies on the assumption that these fluoroesters and the reference

158   organics are removed only by reaction with the oxidant specie (Cl). To verify this

159   assumption, mixtures of oxalyl chloride with N_2 and both organics were prepared and

160   allowed to stand in the dark during two hours. In all cases, the reaction of the organic species

161   with the precursor of Cl(ClC(O)C(O)Cl), in the absence of UV light, was of negligible

162   importance over the typical time periods used in this work. It has been realized test for

163   possible photolysis of the compounds studied, for this, reactants in nitrogen, in the absence of

164   oxidants, were irradiated using the output of all germicidal lamps surrounding the chamber

165   for 30 min. It was not observed any photolysis of fluoroesters or references. The initial

166   concentration used in the experiments were in the range of 180-200 ppm (1 ppm = 2.46×10^{13}

167   molecule cm^{-3} at 298 K and 760 Torr of total pressure) for fluorinated acrylates or

168   methacrylates. The concentration of ClC(O)C(O)Cl 160 to 180 ppm in around 760 Torr of

169   N_2. A mixture of unsaturated halogenated ester/ ClC(O)C(O)Cl/air were analyzed after

170   irradiation in order to identify the products formed in the reactions studied.

171   Products identification experiments were performed using GC-MS analytical technique, a

172   Shimadzu GC-MS QP 5050 spectrometer equipped with a capillary column ZB-5MS (5%

173   phenyl, 95% dimethylpolysiloxane) of 30 m - 0,25 mm. Gas samples were removed from the

174   Teflon chamber using solid phase microextraction (SPME) as a preconcentration technique of

the analytes. The SPME technique involves the extraction of analytes from the sample matrix using a silica fiber generally cover with an absorbent polymer, followed by desorption of analytes by the temperature on the injection port. In this study we have used the [divinylbenzene/Carboxen/polydimethylsiloxane] (DVB / CAR / PDMS) from Supelco, Bellefonte, PA, USA, indicated for this type of compounds. The exposure time was 1 minute, and 2 minutes of desorption in the injection port. The determinations were carried out under atmospheric conditions. For the Cl atoms reactions mixture of fluorinated ester/ ClC(O)C(O)Cl/air also were flushed into the Teflon bag. The photolysis time was 15 seconds for each experiment. In order to identify carbonyl products, the o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) derivatizing agent was used. The PFBHA reacts with carbonyl compounds forming a stable oxime. A 2 mL aqueous solution of PFBHA (25 mg/mL) was prepared in a 4 mL vial. The PFBHA was loaded on the SPME fiber during 90 seconds by head-space extraction. The fiber-PFBHA was exposed inside the chamber other 60 seconds to produce the oxime on the fiber to be transferred to the GC-MS injector. The desorption time was 2 min at 225°C. The column employed was Zebron ZB-5MS (30 m x 0.25 mm x 0.25 μm). The temperature program was 80°C for 5 min, 100°C for 5 min, 200°C for 15 min to 250°C at a rate of 15°/min for the Cl atoms reactions with fluorinated ester.

3. Materials

The following chemicals with purities declared by the supplier were used : N_2 (AGA, 99.999%), synthetic air (Air Liquide, 99.999%), 2,2,2-trifluoroethylacrylate (Aldrich, 99%), 1,1,1,3,3,3-hexafluoroisopropylacrylate (Aldrich, 99%), 2,2,2-trifluoroethylmethacrylate (Aldrich, 99%), and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (Aldrich, 99%), vinyl propionate (Aldrich, 98%), 2-methyl-3-buten-2-ol (Aldrich, 96%), acrylonitrile (Baker,

199 99.5%),diethyl ether (Fluka, 99%),ethyl acrylate (Aldrich, 99%), oxalyl chloride (Aldrich, 99%), o-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine hydrochloride (Aldrich, 98%).

200 99%), o-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine hydrochloride (Aldrich, 98%).

201

4. Results and discussion

203 Relative rate coefficients for the reactions of Cl atoms with halogenated acrylates or

204 methacrylates were determined. The data were fitted to a straight line by the linear least-

205 squares procedure. The losses of TFEA, HFIA, TFEM and HFIM by Cl atoms are shown

206 with different reference compounds in Figs.1, 2, 3 and 4. For each reaction, four experiments

207 were performed for the rate coefficient determination; nevertheless, only one example is

208 displayed in Figs. 1-4.

209 The data on relative rate coefficients ($k_{\text{Fluorinated ester}}/k_{\text{Reference}}$) and the absolute rate coefficients

210 $k_{\text{Fluorinated ester}}$ at room temperature (298K) are presented in Table 1. The ratios were obtained

211 from the average values using different initial concentrations of the reactants. It is gratifying

212 to note the agreement between the experiments conducted with different reference

213 compounds. The rate coefficients obtained by averaging the values from different

214 experiments were the following:

215 $$k_{\text{Cl+ TFEA}} = (2.41 \pm 0.57) \times 10^{-10} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

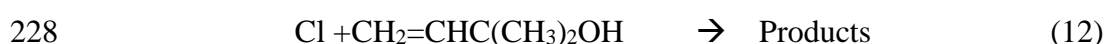216 $$k_{\text{Cl+HFIA}} = (1.39 \pm 0.34) \times 10^{-10} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

217 $$k_{\text{Cl+TFEM}} = (2.22 \pm 0.45) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

218 $$k_{\text{Cl+HFIM}} = (2.44 \pm 0.52) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

219 The errors quoted are twice the standard deviation arising from the least squares fit of the

220 straight lines, to which we have considered also the corresponding error on the reference rate

221 coefficients.

222   The following compounds were used as reference reactions: acrylonitrile, ethyl acrylate,

223   vinyl propionate, 2-methyl-3-buten-2-ol and diethyl ether to determine the rate coefficient of

224   the reactions (1) to (4):

225   $$Cl + CH_2=CHCN \qquad \rightarrow \quad Products \qquad (9)$$

226   $$Cl + CH_2=CHC(O)OCH_2CH_3 \rightarrow \quad Products \qquad (10)$$

227   $$Cl+CH_3CH_2C(O)OCH=CH_2 \rightarrow \quad Products \qquad (11)$$

228   $$Cl +CH_2=CHC(CH_3)_2OH \quad \rightarrow \quad Products \qquad (12)$$

229   $$Cl + (C_2H_5)_2O \qquad \rightarrow \quad Products \qquad (13)$$

230   Where k_9= $(1.11\pm 0.23) \times 10^{-10}$ (Teruel et al., 2007), k_{10}= $(2.53\pm 0.46) \times 10^{-10}$ (Teruel et al.,

231   2009), k_{11}= $(2.06 \pm 0.36) \times 10^{-10}$ (Teruel et al., 2009), k_{12}= $(3.00\pm 0.41) \times 10^{-10}$ (Takahashi et

232   al., 2010), k_{13}= $(2.54\pm 0.18) \times 10^{-10}$ (Nelson et al., 1990). All the k values are in units of cm^3

233   $molecule^{-1}$ s^{-1}. To the best of our knowledge, there are no other prior reported values of the

234   rate coefficients for the reactions (1) to (4) of Cl atoms with halogenated unsaturated esters.

235   Thus, the present work is the first kinetic study of these reactions and therefore no direct

236   comparison with the literature could be made.

237   However, it is interesting to compare the rate coefficients of the reactions of Cl atoms with

238   unsaturated esters with those that have fluorine substitution in the molecule in order to

239   rationalize the effect of substituents on the reactivity of the esters toward Cl atoms.

240   **4.1. Reactivity trends**

241   Table 2 shows a comparison between the rate coefficients of the reactions of OH radicals and

242   Cl atoms with a series of unsaturated esters and the kinetic data obtained in this study for

243   halogenated unsaturated esters. With regard to OH radicals reactions, it is possible to observe

244   generally that when H atoms are replaced by F atoms the rate coefficient values decrease:

245   $k_{CH2=CHC(O)OCH2CH3 + OH}$= $(1.70 \pm 0.40) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} > $k_{CH2=CHC(O)OCH2CF3 + OH}$=

246   $(1.25 \pm 0.13) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, $k_{CH2=C(CH3)C(O)OCH2CH3 + OH}$= $(4.58 \pm 0.59) \times 10^{-11}$ cm^3

247   molecule^{-1} s^{-1} > $k_{CH2=C(CH3)C(O)OCH2CF3 + OH}$= (2.54 ± 0.12) × 10^{-11} cm^3 molecule^{-1} s^{-1},

248     $k_{CH2=C(CH3)C(O)OCH(CH3)2 + OH}$=(2.28 ± 0.25) × 10^{-11} cm^3 molecule^{-1} s^{-1} > $k_{CH2=C(CH3)C(O)OCH(CF3)2 +}$

249     $_{OH}$= (1.41 ± 0.11) × 10^{-11} cm^3 molecule^{-1} s^{-1}. This difference can be attributed to the negative

250   inductive effect of the F atoms substituents (Hurley et al., 2007), therefore the –CF$_3$ group

251   reduces the partial negative charge, then electrophilic addition of OH radicals to the double

252   bond in halogenated esters is less favored compared to the addition to non-halogenated

253   unsaturated esters. On the other hand, for Cl atoms reactions, the rate coefficients of

254   unsaturated and non-halogenated esters are similar to the halogenated and unsaturated esters

255   within experimental uncertainties. Therefore, the effect of –F atoms substituents on the

256   reactivity of the double bond for Cl atoms is less important than the effect observed with OH

257   addition, probably because the reactions with Cl atoms, in general, are less selective than the

258   reaction in organic compounds with OH radicals (Bravo et al, 2013). The rate coefficients

259   values reported in this work for the reactions studied are in close agreement with the rate

260   coefficients of Cl atoms with similar unsaturated esters. Rodríguez et al., have reported

261   values (in units of cm^3 molecule^{-1} s^{-1}) for the rate coefficients of Cl + allyl trifluoroacetate

262   and Cl + vinyl trifluoroacetate reactions of (1.75 ± 0.21) × 10^{-10} and (2.08 ± 0.16) × 10^{-10},

263   respectively using a 200 L Teflon bag and GC-FID as detection system (Rodríguez et al.,

264   2016).

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266   **4.2. Products identification study**

267   In addition to the kinetic study, the products of the reaction of halogenated esters studied in

268   this work with Cl atoms were identified and the gas phase mechanisms were postulated.

269   For the compounds under study, Cl atoms reactions proceed mainly by initial addition of Cl

270   to the >C=C< bond and, in absence of NOx, the alkyl radicals formed react with O$_2$ to lead

271   peroxy radicals. These peroxy radicals will undergo self- and cross-peroxy reactions which

272   will result, in the formation of 1,2-chloroalkoxy radicals (Calvert et al., 2000). This behavior

273   has also been observed in the reaction with Cl atoms with unsaturated halogenated esters

274   (Rodríguez et al., 2016).

275   The 1,2-chloroalkoxy radicals can lead the formation of final products by different pathways:

276   Simplified exemplary reaction mechanisms for the addition reactions of Cl atoms with the

277   halogenated acrylates and methacrylates in the absence of NO_x are shown in Figures 5 and 6,

278   respectively.

279   **Cl reaction with TFEA and HFIA**

280   Regarding to the reaction of Cl atoms with acrylates, possible fates of the chloroalkoxy

281   radicals formed includes:

282   i)   Reaction with O_2 to give $CF_3RCHOC(O)C(O)CH_2Cl$ and $HO_2^{\bullet}$ radical.

283   ii) Chloroalkoxy radical scission between C_2 and C_3, to give $HC(O)CH_2Cl$ and

284                $CF_3RCHOC(O)C(O^{\bullet})$ radical.

285   iii) Chloroalkoxy radical scission between C_1 and C_2, to give $CF_3RCHOC(O)CHO$ and

286                $HC^{\bullet}(Cl)H$ radical.

287   In the reaction of acrylates with Cl atoms we observed trifluoroacetaldehyde ($CF_3C(O)H$) as

288   unique product of reaction of TFEA with Cl atoms. This could be explained by considering

289   the addition of Cl to the double bond $>C=C<$. $CF_3C(O)H$ was observed in our experimental

290   conditions and using the derivatizing agent o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine

291   hydrochloride (PFBHA) to monitor carbonyl compounds. The presence of

292   trifluoroacetaldehyde was observed with fragments of m/z 293 (for trifluoroacetaldoxime),

293   181 and 44 (see Figure 5 channel ii). An example of the chromatogram obtained is shown in

294   Fig. 7. On the other hand, it could not be observed any product formation in the reaction of

295   HFIA with Cl atoms in our experimental conditions.

Cl reaction with TFEM and HFIM

Regarding to the reaction of Cl with methacrylates, possible fates of the chloroalkoxy radicals formed includes:

    i)   -CH_3 elimination to give $CF_3RCHOC(O)C(O)CH_2Cl$ and $CH_3^{\bullet}$ radical.

    ii) Chloroalkoxy radical scission between C_2 and C_3, to give $CF_3RCHOC(O)C(O^{\bullet})$ radical and $CH_3C(O)CH_2Cl$.

    iii) Chloroalkoxy radical scission between C_1 and C_2, to give $CF_3RCH_2OC(O)C(O)CH_3$ and $HC^{\bullet}(Cl)H$ radical.

From the analysis of the chromatogram obtained by GC-MS, it could be observed the formation of chloroacetone ($CH_3C(O)CH_2Cl$) and formaldehyde (HCOH) as products of the reaction of methacrylates with Cl atoms with the fraction m/z= 43 characteristic of the chloroacetone. Chloroacetone is produced through, C-C scission (see Figure 6 channel ii). In our experimental conditions and using the derivatizing agent *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) to monitor carbonyl compounds, we have observed the presence of formaldehyde solely in the reactions of Cl atoms with the fluorinated methacrylates. In this case, the presence of formaldehyde was observed with fragments of m/z 225 (for formaldoxime), 181 and 44 (see Figure 6 channel i). These results are in agreement a previous work performed by in situ FTIR for the reaction of methyl methacrylate with Cl atoms (Blanco et al., 2011), where it was observed chloroacetone and formaldehyde with yields of of (41 ± 6) % and (23 ± 3) %, respectively. An example of the chromatogram obtained is shown in Fig. 8. Formyl chloride and methyl pyruvate, coproducts reported in the study of nonfluorinated methacrylates, have not been observed in the present experiments.

5. Atmospheric implications

Tropospheric lifetimes, τ_x, of the halogenated acrylates and methacrylates studied in this work were calculated through the expression: $\tau_x = 1/k_x[X]$ with X = Cl. Table 3 lists the atmospheric lifetimes with respect to the reaction with Cl atoms and OH radicals obtained in our previous work (Tovar and Teruel, 2014) for comparative purposes. In the case of Cl reactions, these calculations were performed, considering a global average chlorine concentration of 1×10^4 atoms cm^{-3} (Wingenter et al., 1996). We can observe that the reactions of the halogenated esters with Cl atoms are between 5 and 8 days, this will probably have important impact in coastal areas (Thornton et al., 2010). Regarding to reactions with OH radicals, the atmospheric lifetimes are between 5 and 11 hours. Furthermore, the atmospheric lifetimes with O$_3$ molecules have been calculated using the 'Environmental Protection Agency' rate constant calculation software, AOPWINv1.91 (17) being obtained an atmospheric lifetime between 1 and 7 days. Unfortunately, no kinetic data are available for the reaction of these compounds with NO$_3$ radicals. The short lifetimes calculated for these compounds indicate that they could degraded close to the emission source areas, causing a local impact potentially leading photo-oxidants in the atmosphere, responsible for the formation of photochemical smog. It is possible to observe that the main tropospheric degradation pathway for the compounds studied is the reaction with OH radical. Although, in marine and certain polluted continental areas where the Cl atoms concentration can reach levels of 1×10^5 or more, Cl-atom initiated reactions could compete with the OH reaction (Singh et al., 1996; Riedel et al., 2013). Halogenated products of these reactions studied, such as halogenated glyoxylates and pyruvates, could then react with the OH radical or Cl atoms to generate fluorinated aldehydes that could contribute to the formation of ozone and secondary organic aerosols (SOA) (Ofner et al., 2013; Zhang et al., 2017). The interactions with SOA occur in the gas phase and in the particle phase, it is known that halogens are involved in the

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345   ageing process of organic aerosols (Kroll et al., 2011). In our experimental results,

346   chloroacetone has been identified as reaction product of TFEM and HFIM with Cl, although

347   the main oxidant of this compound in the atmosphere is the OH radical, it is known that its

348   reaction with Cl atoms can generate compounds as HCl and HCOCl (Carr et al., 2003). On

349   the other hand, halogenated formaldehyde formed in atmospheric degradation of VOCs is one

350   the most reactive and important species in tropospheric photochemistry and ozone formation

351   (Graedel, 1978). It has been observed that atmospheric lifetimes are rather short, therefore, it

352   is expected that it will contribute significantly to the formation of ozone and other

353   photooxidants in the atmosphere near their emission source. For this reason, the ozone

354   photochemical potential (POCP) could be used as a modeling method to estimate the

355   potential of ozone creation of VOCs relative to that of ethene which is given the value

356   100 (Derwent et al., 2007; Jenkin et al., 1998). This estimated method gives values of POCP

357   for TFEA, HFIA, TFEM and HFIM around, 36, 28, 90, and 42 respectively. It can be

358   observed that, in relation to ethene as reference compound, the TFEM could contribute

359   significantly to the formation of tropospheric ozone. Formaldehyde (HCHO) is observed in

360   the atmospheric degradation of halogenated methacrylates, with a ε^{POCP} of 119 (Derwent et

361   al., 2007). It is known that, this small aldehyde is one of the most reactive and most important

362   species in tropospheric photochemistry and ozone formation (Calvert et al., 2011). In

363   addition, it is necessary to mention that Cl-initiated oxidation could be of equal importance to

364   OH radicals, mainly in regions with high emissions, such as coastal and marine areas. In such

365   cases, the chemistry of Cl should also be considered, and this may lead to an increase of ε^{POCP}

366   values.

367   Moreover, it is important to mention that one of the environmental problems today is that of

368   acid rain [21]. Although H_2SO_4, HNO_3 and HCl are the most relevant acid species in the

369   atmosphere, it is important to note that the tropospheric oxidation of VOCs containing Cl, F,

370   N or S in their chemical structures could contribute significantly to atmospheric acidification

371   [22]. In accordance with the above an Acidification Potential "AP" can be defined as the

372   number of acid equivalent potentials (H^+) per unit mass of a given compound X with respect

373   to the number of H^+ per unit mass of the reference compound, with SO_2 being the proposed

374   gas reference. The number of acid equivalent potentials in molecule X can be obtained by the

375   number of Cl, F, N atoms and 2 times the number of S atoms present in the structure. Thus,

376   the AP for X related to SO_2 is given by (de Leeuw , 1993):

377    $$AP\text{Unsaturated ester} = \frac{M\,SO2}{M\,\text{Unsaturated ester}} \times \frac{nCl + nF + nN + 2.nS}{2} \quad (14)$$

378   Where M_{SO2} and $M_{\text{Unsaturated ester}}$ are the molecular weights of the reference compound (sulfur

379   dioxide) and the compound in study respectively, and n_x number of atoms of Cl, F, N and S

380   present in the unsaturated ester structure. Analysis of potential acidification indicated in

381   Table 3, show that the capacity of acidifying of the unsaturated halogenated esters are close

382   to the SO_2 (between 0.57 to 0.81) . This indicates that these compounds and their atmospheric

383   degradation products could be involved in harmful "acid rain" events that are recorded in

384   polluted atmospheres, if they are removed from the air by wet deposition processes.

385   In conclusion, the compounds studied have shorts atmospheric lifetimes and it is known that,

386   homologous halogenated unsaturated esters which have been studied recently have short

387   lifetime and low GWP, so they are expected to have a minor impact on global warming and

388   climate change (Rodríguez et al., 2016). In addition, ε^{POCP} is relatively low, so compounds

389   are expected to have no significant local effects on ozone formation, except in areas with

390   increased levels of Cl atoms where their chemistry could increase local ozone formation. In

391   relation to the products, it is expected that halogenated carboxylic compounds generated by

392   the oxidation of halogenated methacrylates and acrylates could removed by heterogeneous

393   processes, contributing to the acidification of precipitation, producing harmful effects in both

394   humans and biota.

Acknowledgements

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Figure captions

Fig. 1: Relative kinetic plot of the reaction of Cl atoms with TFEA using Acrylonitrile (■) and Ethyl acrylate (▲) as references at 298K and 760 Torr.

Fig. 2: Relative kinetic plot of the reaction of Cl atoms with HFIA using Acrylonitrile (■) and Vinyl Propionate (●) as references at 298K and 760 Torr.

Fig. 3: Relative kinetic plot of the reaction of Cl atoms with TFEM using (■) 2-Methyl-3-buten-2-ol and Vinyl Propionate (●) as references at 298K and 760 Torr.

Fig. 4: Relative kinetic plot of the reaction of Cl atoms with HFIM using (■) Acrylonitrile and Diethyl ether (●) as references at 298K and 760 Torr.

Fig. 5: Simplified mechanism for the Cl atom initiated oxidation of TFEA and HFIA via addition of Cl the double bond. The identified products are shown in filled line in the reaction between TFEA and Cl atoms.

Fig. 6: Simplified mechanism for the Cl atom initiated oxidation of TFEM and HFIM via addition of to the terminal carbon of the double bond. The identified products are shown in filled line, which were observed in both reactions studied.

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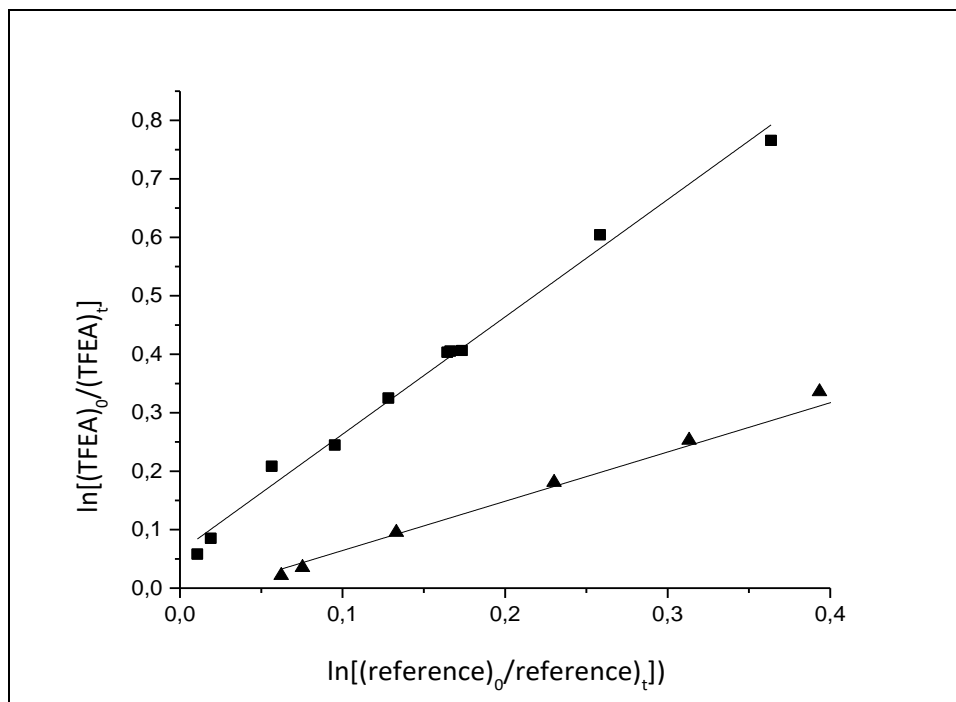
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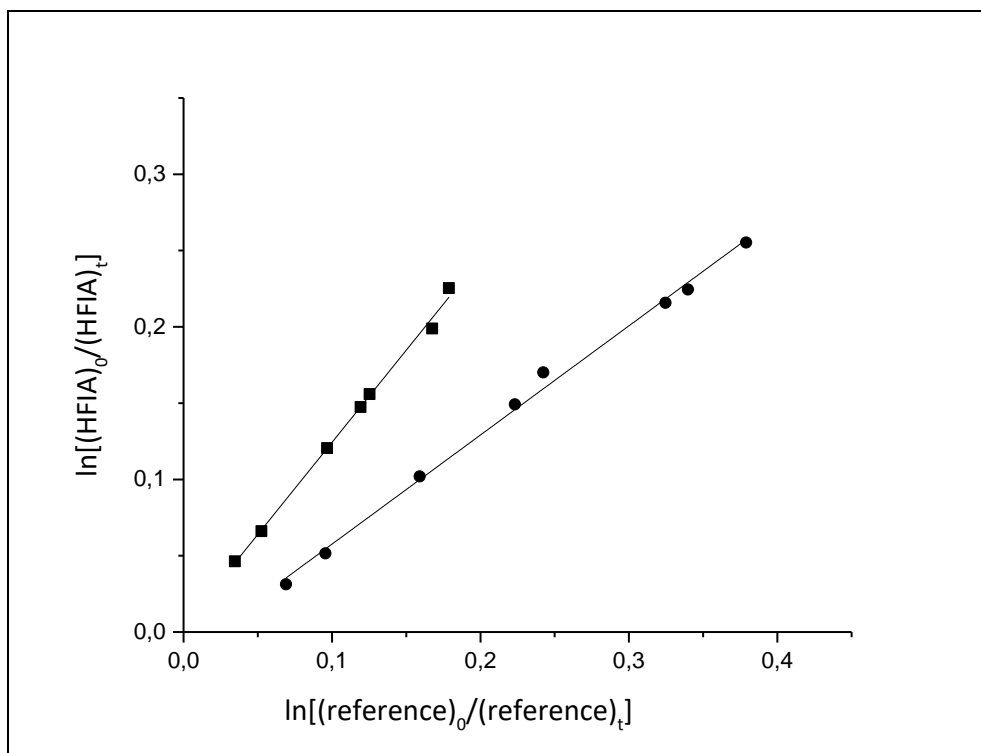
Fig. 2

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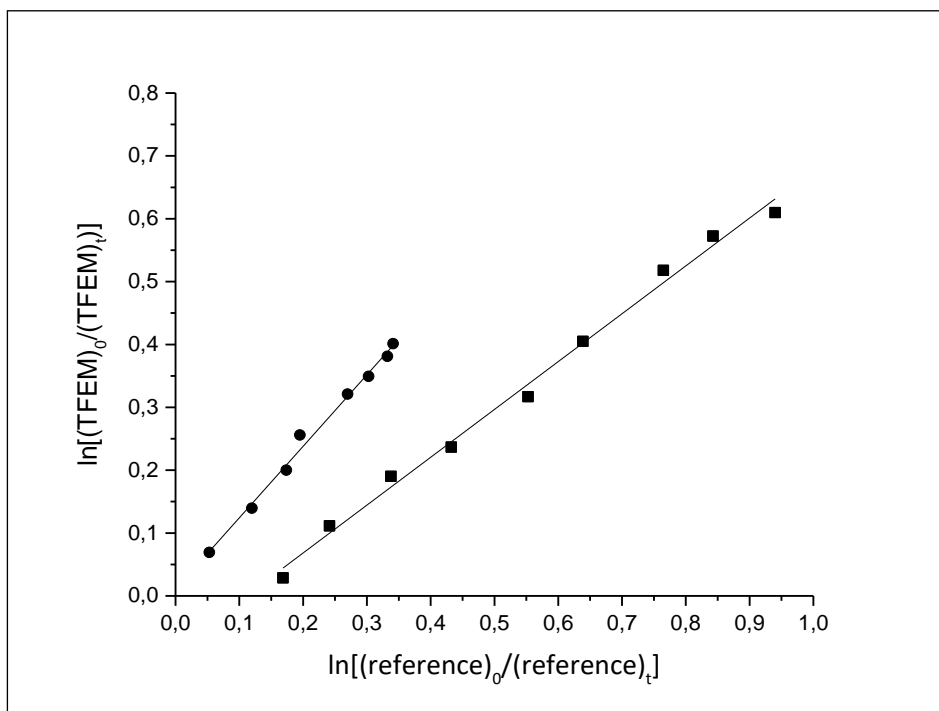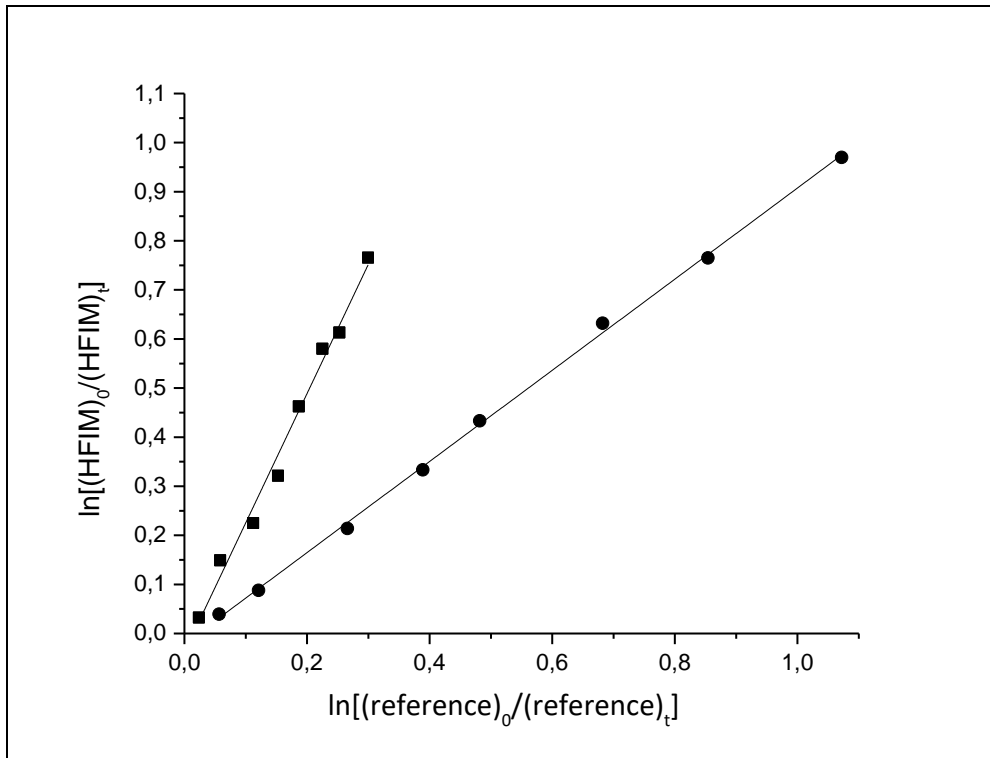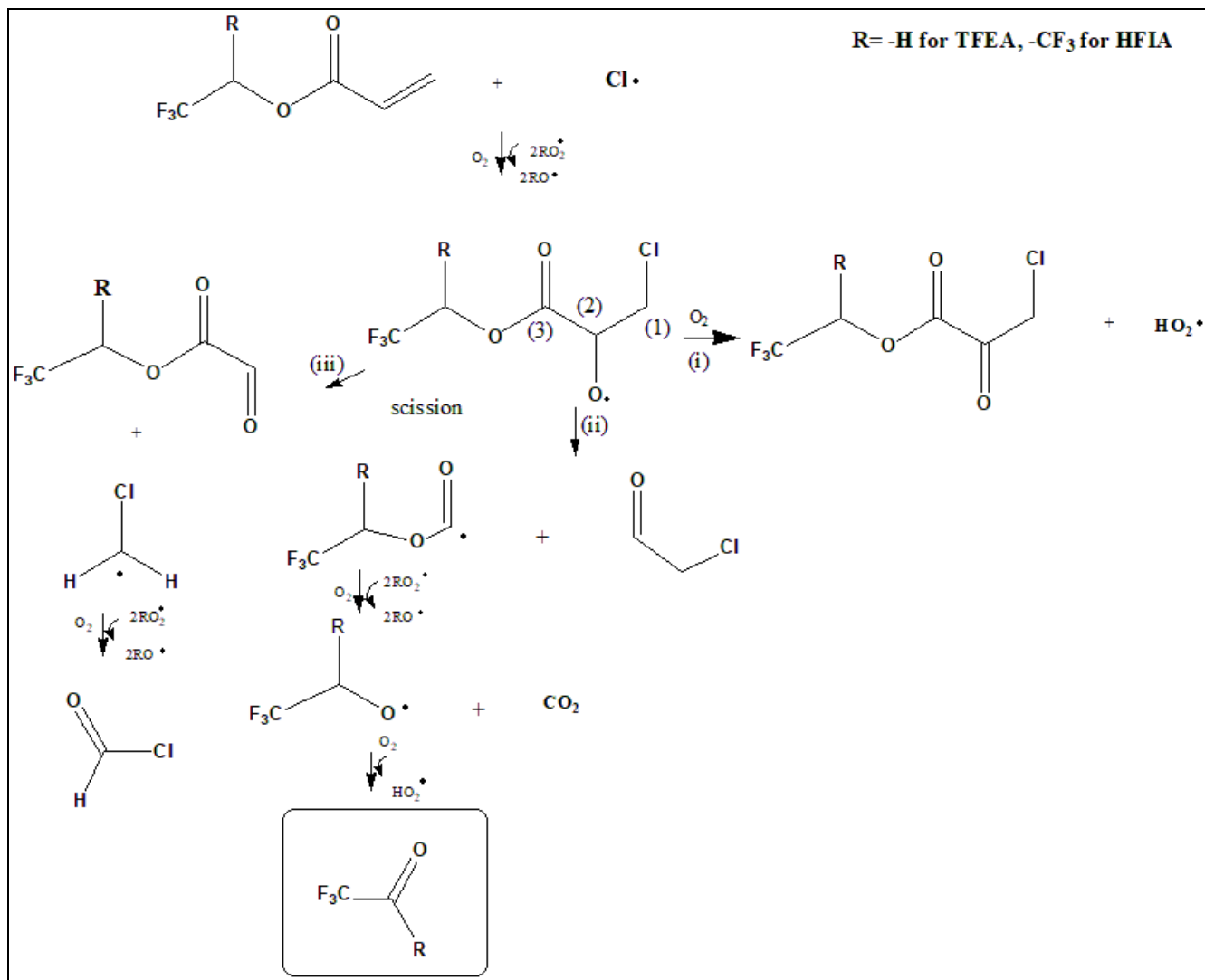696
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Fig. 3

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Fig. 4

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Fig. 5

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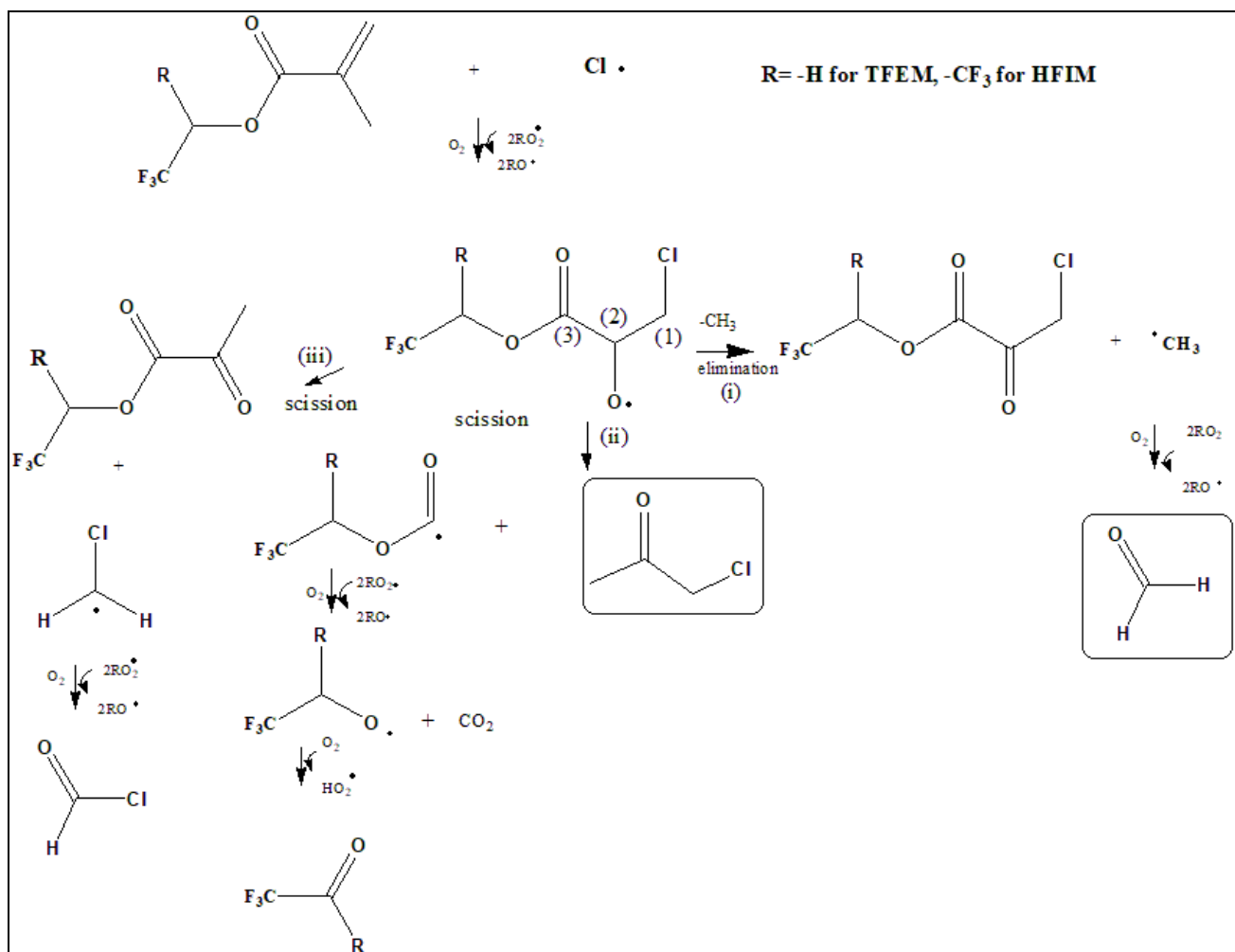
Fig. 6.

Table 1
Reference compound, measured rate coefficient ratios, $k_{\text{Fluorinated ester}}/k_{\text{reference}}$, and the obtained rate coefficients for the reactions of Cl atoms with TFEA, HFIA, TFEM and HFIM at 298 K in 760 Torr of nitrogen.

Fluorinated ester	Reference	$k_{Fluorinated}$ $_{ester}/k_{Reference.}$	k(cm^3 molecule^{-1}s^{-1})
CH_2=CHC(O)OCH$_2$CF$_3$ + Cl	Acrylonitrile	(1.95±0.01)	(2.16±0.24)×10^{-10}
	Acrylonitrile	(2.19±0.06)	(2.43±0.57)×10^{-10}
	Ethyl acrylate	(0.93±0.01)	(2.35±0.45)×10^{-10}
	Ethyl acrylate	(1.07±0.02)	(2.71±0.54)×10^{-10}
	Average		**(2.41±0.57)×10^{-10}**
CH_2=CHC(O)OCH(CF$_3$)$_2$+ Cl	Acrylonitrile	(1.24±0.01)	(1.38±0.29)×10^{-10}
	Acrylonitrile	(0.97±0.02)	(1.08±0.24)×10^{-10}
	Vinyl Propionate	(0.73±0.02)	(1.50±0.30)×10^{-10}
	Vinyl Propionate	(0.77±0.03)	(1.59±0.34)×10^{-10}
	Average		**(1.39±0.34)×10^{-10}**
	2-Methyl-3-buten-2-ol	(0.73±0.02)	(2.19±0.36)×10^{-10}

CH$_2$=C(CH$_3$)C(O)OCH$_2$CF$_3$+ Cl	2-Methyl-3-buten-2-ol	(0.78±0.01)	(2.34±0.35)×10^{-10}
	Vinyl Propionate	(1.14±0.02)	(2.35±0.45)×10^{-10}
	Vinyl Propionate	(0.97±0.02)	(2.00±0.39)×10^{-10}
	Average		**(2.22±0.45)×10^{-10}**
CH$_2$=C(CH$_3$)C(O)OCH(CF$_3$)$_2$+ Cl	Diethyl ether	(0.98±0.04)	(2.48±0.28)×10^{-10}
	Diethyl ether	(0.92±0.01)	(2.33±0.19)×10^{-10}
	Acrylonitrile	(1.97±0.05)	(2.18±0.44)×10^{-10}
	Acrylonitrile	(2.58±0.06)	(2.78±0.52)×10^{-10}
	Average		**(2.44±0.52)×10^{-10}**

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

VOC	k_{OH}(cm^3 molecule^{-1}s^{-1})	k_{Cl}(cm^3 molecule^{-1}s^{-1})
CH$_2$=CHC(O)OCH$_2$CF$_3$	$(1.25 \pm 0.13) \times 10^{-11}$[a]	**$(2.41 \pm 0.57) \times 10^{-10}$[b]**
CH$_2$=CHC(O)OCH$_2$CH$_3$	$(1.70 \pm 0.40) \times 10^{-11}$[c]	$(2.53 \pm 0.46) \times 10^{-10}$[d]
CH$_2$=CHC(O)OCH(CF$_3$)$_2$	$(1.41 \pm 0.11) \times 10^{-11}$[a]	**$(1.39 \pm 0.34) \times 10^{-10}$[b]**
CH$_2$=CHC(O)OCH(CH$_3$)$_2$	-	-
CH$_2$=C(CH$_3$)C(O)OCH$_2$CF$_3$	$(2.54 \pm 0.12) \times 10^{-11}$[a]	**$(2.22 \pm 0.45) \times 10^{-10}$[b]**
CH$_2$=C(CH$_3$)C(O)OCH$_2$CH$_3$	$(4.58 \pm 0.59) \times 10^{-11}$[e]	$(2.71 \pm 0.21) \times 10^{-10}$[f]
CH$_2$=C(CH$_3$)C(O)OCH(CF$_3$)$_2$	$(1.65 \pm 0.14) \times 10^{-11}$[a]	**$(2.44 \pm 0.52) \times 10^{-10}$[b]**
CH$_2$=C(CH$_3$)C(O)OCH(CH$_3$)$_2$	$(2.28 \pm 0.25) \times 10^{-11}$[g]	$(2.50 \pm 0.78) \times 10^{-10}$[g]

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803 [a] (Tovar and Teruel, 2014)
804 **[b] This work.**
805 [c] (Teruel et. al, 2006)
806 [d] (Teruel et. al, 2009)

[e] (Blanco et. al, 2006)
[f] (Porrero et. al, 2010)
[g] (Blanco et. al, 2009)

Table 3

Estimated tropospheric lifetimes of the halogenates acrylates and methacrylates studied in this work with different troposphere oxidants.

VOC	τ_{OH}[a]	τ_{Cl}[b]	τ_{O3}[c]
TFEA	11 hours	5 days	7 days
HFIA	10 hours	8 days	7 days
TFEM	5 hours	5 days	1 days
HFIM	8 hours	5 days	1 days

[a] (Tovar and Teruel, 2014)
[b] This work.
[c] (US Environmental Protection Agency, 2000)

Table 4

Potential for acidification of unsaturated halogenated esters studied and SO_2 as reference.

Unsaturated fluoroester	Molecular Weights	n_{total}	AP
$CH_2=CHC(O)OCH_2CF_3$	154	3	0.62
$CH_2=CHC(O)OCH(CF_3)_2$	222	6	0.86
$CH_2=C(CH_3)C(O)OCH_2CF_3$	168	3	0.57
$CH_2=C(CH_3)C(O)OCH(CF_3)_2$	236	6	0.81
SO_2	64		1