Chemical Physics Letters 578 (2013) 33–37

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Tropospheric degradation of 2,2,2 trifluoroethyl butyrate: Kinetic study of their reactions with OH radicals and Cl atoms at 298 K

María B. Blanco [a], Cynthia Rivela [a,b], Mariano A. Teruel [a,*]

[a] Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

[b] Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Asunción, Campus Universitario, San Lorenzo, Paraguay

ARTICLE INFO

Article history:
Received 28 March 2013
In final form 7 June 2013
Available online 14 June 2013

ABSTRACT

Rate coefficients of the reactions of OH radicals and Cl atoms with 2,2,2 trifluoroethyl butyrate have been determined at 298 K and atmospheric pressure. The decay of the organics was followed using a gas chromatograph with a flame ionization detector (GC-FID) and the rate coefficients were determined using the relative rate method. This is the first kinetic study for these reactions under atmospheric pressure. The kinetic data are used to update the correlation k_{OH} *vs.* k_{Cl} for different fluoroesters, to develop reactivity trends in terms of halogen substitution and to estimate the tropospheric lifetime of 2,2,2 trifluoroethyl butyrate.

1. Introduction

It is well known the effort to replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) due to their significant role in stratospheric ozone depletion [1]. In this sense, the new alternatives must have similar properties to CFCs but without the harmful effects to the environment such as ozone layer depletion and global warming potentials [2].

Hydrofluoroethers (HFEs), are considered good candidates for these replacements, by the insertion of an ether oxygen atom into the molecule that modifies the thermo-physical properties of the compound for specific end-uses and to activate the molecule towards troposheric oxidant attack. This leads to significantly shorter atmospheric lifetimes when compared to hydrofluorocarbons (HFCs), decreasing with the number of hydrogen atoms in the molecule. The main fate of HFEs in the atmosphere is reaction with OH radicals forming the corresponding hydrofluorinated esters (FESs) [3,4]. Hence, for a complete assessment of the atmospheric chemistry and potential detrimental environmental impacts of HFEs, it is necessary to understand the atmospheric chemistry of FESs. As for HFEs, FESs are removed from the troposphere mainly by reaction with OH radicals [5] with possible contributions from wet and dry deposition and reaction with Cl atoms in marine environments and heavily industrialized urban areas with high levels of chloride-containing aerosol [6]. The tropospheric degradation of FESs may contribute to the environmental burden of trifluoroacetic acid (TFA) or derivatives [7,8].

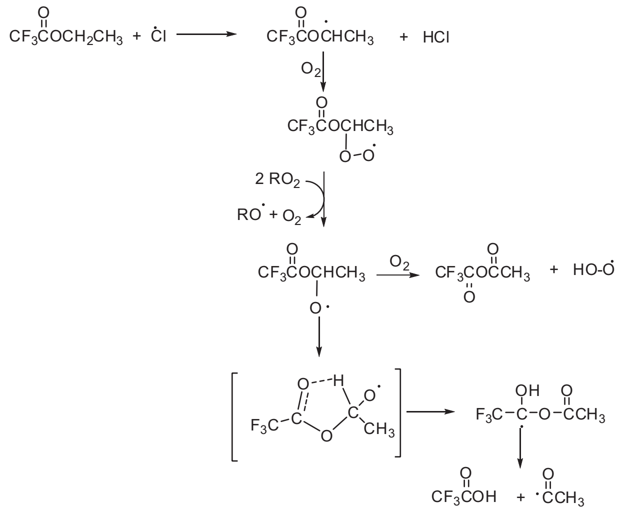
In order to evaluate the possible contribution of the photooxidation of FESs to TFA formation or derivates in the environment, it is necessary to know the rate coefficients for the reactions of FESs with tropospheric oxidants such as OH radicals or Cl atoms, as well as the associated degradation pathways and product distribution.

In these sense, we have performed previous relative kinetic studies of the degradation of fluoroacetates (methyl trifluroacetate, ethyl trifluoroacetate, methyl difluoroacetate and 2,2,2-trifluoroethyl 2,2,2-trifluoroacetate) initiated by OH-radicals by the GC-FID technique [5] and an FTIR study of the Cl-atom degradation of these compounds in a quartz glass photoreactor [6]. In addition, previous product studies were conducted for the Cl initiated oxidation of methyl trifluoroacetate, ethyl trifluoroacetate and methyl difluoroacetate [7]. The fate of the fluoroalkoxy radicals formed in these reactions has been postulated to mainly occurs through (i) an H-atom abstraction by reaction with O_2, to produce the corresponding fluoroanhydride and (ii) an α-ester rearrangement via a five-membered ring intermediate to give the corresponding fluoroacetic acid.

---

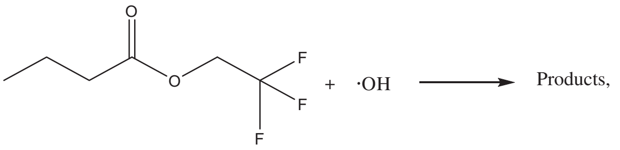
* Corresponding author. Fax: +54 351 4334180.
E-mail address: mteruel@fcq.unc.edu.ar (M.A. Teruel).

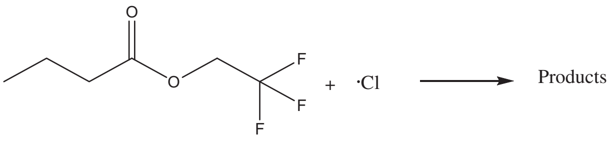
0009-2614/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2013.06.004



The product distribution and the mechanism of the reaction of Cl atoms with 2,2,2-trifluoroethyl 2,2,2-trifluoroacetate ($CF_3C(O)OCH_2CF_3$) were investigated in a separate study [8] using the same experimental technique at NOx-free conditions. The formation of the corresponding anhydride, CF_2O and CO was identified and no trifluoroacetic acid (TFA) formation was observed. The negligible importance of the α-ester channel to produce TFA was explained by the reduction of the stability of the five-membered transition state of the α-ester rearrangement.

In a continuation of our investigations on the OH-radical and Cl-atom initiated photooxidation of these fluoroacetates [5–8], we present here room temperature relative kinetic determinations of the rate coefficients for the following reactions performed in a collapsible Teflon photoreactor at atmospheric pressure of nitrogen:

 (1)

 (2)

To the best of our knowledge, this work provides the first kinetic study for the reaction of OH radicals and Cl atoms with 2,2,2-trifluoroethyl butyrate (TFEB). Therefore, this is the first determination of the rate coefficients of the reactions (1) and (2) under atmospheric conditions. The aim of this study was to extend the existing limited kinetic data base of the reactions of OH radicals and Cl atoms with fluoroesters as part of ongoing work in our laboratory regarding the atmospheric impact of volatile organic compounds (VOCs) as acceptable candidates to replace the harmful CFCs and their derivatives in industrial uses. In this sense, the results are discussed in terms of the halogen substituents effects on the reactivity of the esters studied and a correlation between k_{OH} *vs.* k_{Cl} of different halogenated VOCs, including FES, is developed.

Atmospheric lifetimes of the 2,2,2-trifluoroethyl butyrate studied, with respect to reaction with OH and Cl, have been calculated using the rate coefficients obtained in this Letter.

2. Experimental

All experiments were carried out in an 80 L collapsible Teflon bag at (296 ± 2) K and atmospheric pressure (760 Torr). Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in nitrogen, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of zero grade N_2 and the bag was then filled with the zero grade N_2 or synthetic air. Before each set of experiments, the Teflon bag was cleaned by filling it with a mixture of O_2 and N_2 which was photolyzed for 15–25 min using four germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O_3.

After this procedure, the bag was cleaned again by repeated flushing with N_2 and, before performing the experiments, gas chromatography was used to verify that there were no observable impurities.

H_2O_2 and ClC(O)C(O)Cl, were used to generate OH radicals and Cl atoms, respectively, by direct UV photolysis with germicidal lamps emitting at 254 nm (Philips 30 W). The reaction mixtures were removed from the Teflon bag using calibrated gas syringes. The organics 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 200 °C for these compounds.

In the presence of hydroxyl radicals and chlorine atoms, 2,2,2 trifluoroethyl butyrate and the reference compounds decay through the following reactions:

$$X + \mathrm{TFEB} \rightarrow \mathrm{Products}, \tag{3}$$

$$X + \mathrm{Reference} \rightarrow \mathrm{Products} \tag{4}$$

where X = OH or Cl.

The relative rate technique relies on the assumption that 2,2,2 trifluoroethyl butyrate and reference are removed solely by reaction with OH radicals or Cl atoms.

Provided that the reactant and reference compound are lost only by reactions (3) and (4), then it can be shown that:

$$\ln\left\{\frac{[\mathrm{TFEB}]_0}{[\mathrm{TFEB}]_t}\right\} = \frac{k_3}{k_4}\ln\left\{\frac{[\mathrm{Reference}]_0}{[\mathrm{Reference}]_t}\right\} \tag{I}$$

where $[\mathrm{TFEB}]_0$, $[\mathrm{Reference}]_0$, $[\mathrm{TFEB}]_t$ and $[\mathrm{Reference}]_t$ are the concentrations of TFEB and reference compound at times t_0 and t, respectively, and k_3 and k_4 are the rate constants of reactions (3) and (4), respectively.

By using this technique, the rate constants for the reactions (1) and (2) were obtained from Eq. (I). The data were fitted to a straight line by the linear least-squares procedure. Mixtures of H_2O_2 or ClC(O)C(O)Cl with both organics were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the radical precursor, in the absence of UV light, was of negligible importance over the typical time periods used in this work. Additionally, to test for possible photolysis of the reactants used, mixtures of the reactants in nitrogen or synthetic air, in the absence of H_2O_2 or ClC(O)C(O)Cl, were irradiated using the output of all the germicidal lamps surrounding the chamber between 30 and 50 min. No significant (<2%) photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 224–262 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) for 2,2,2 trifluoroethyl butyrate, ethyl acetate, cyclohexane and acrylonitrile, 50–130 ppm for H_2O_2 and 190–220 ppm for ClC(O)C(O)Cl.

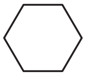
3. Materials

The chemicals used were N_2 (AGA, 99.999%), synthetic air (AGA, 99.999%), 2,2,2 trifluoroethyl butyrate (Aldrich, 98%), ethyl acetate (Aldrich, 99%), cyclohexane (Merck, 99%), acrylonitrile (Baker, 99.5%), hydrogen peroxide (Ciccarelli, 60% wt) and oxalyl chloride (Aldrich, 98%). TFEB and reference compounds were degassed by repeated freeze-pump-thaw cycling.

4. Results

Figures 1 and 2 show the plot of ln([TFEB]$_0$/[TFEB]$_t$) *vs.* ln([Reference]$_0$/[Reference]$_t$), for reactions (1) and (2) using ethyl acetate, cyclohexane and acrylonitrile as reference compounds. For the reactant studied, four runs, using two different references, were performed for the rate coefficient determination; however, for the sake of clarity, only one example is presented in Figures 1 and 2. The following compounds were used as reference reactions to determine the rate coefficient of reactions (1) and (2):

$$OH + CH_3C(O)OCH_2CH_3 \rightarrow \text{Products} \quad (5)$$

OH +  → Products, (6)

$$Cl + CH_3C(O)OCH_2CH_3 + CH_3C(O)OCH_2CH_3 \rightarrow \text{Products} \quad (7)$$

$$Cl + CH_2{=}CHCN \rightarrow \text{Products} \quad (8)$$

where $k_5 = (1.79 \pm 0.16) \times 10^{-12}$ [9], $k_6 = (6.38 \pm 1.28) \times 10^{-12}$ [10], $k_7 = (1.76 \pm 0.26) \times 10^{-11}$ [11] and $k_8 = (1.1 \pm 0.2) \times 10^{-10}$ [12]. All the k values are in units of cm^3 molecule^{-1} s^{-1}.

Both plots show practically zero intercepts and good linearity and suggest that the contribution of the secondary reactions with the products of the reactions studied here could be considered negligible. The ratio of the rate coefficients was calculated from the experimental data using Eq. (I) from the slopes of the plots shown in Figures 1 and 2.

The rate coefficients for reactions (1) and (2), k_1 and k_2, were obtained from the ratio $k_{TFEB}/k_{Reference}$ as the value of $k_{Reference}$ was known.

The ratio of the rate coefficients, k_1/k_5, k_1/k_6, k_2/k_7 and k_2/k_8 and the corresponding rate coefficients for the reactions of OH radicals and Cl atoms with 2,2,2 trifluoroethyl butyrate, are presented in Table 1. The ratios were obtained from the average of several experiments using different initial concentrations of the reactants. It is gratifying to note the agreement between the experiments conducted with two different reference compounds.

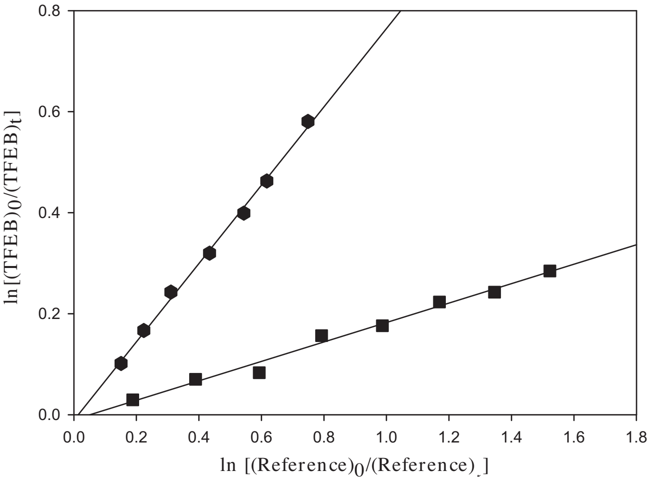


Figure 1. Relative rate data for the reaction of OH with 2,2,2-trifluoroethyl butyrate using ethyl acetate (●) ($r^2 = 0.996$) and cyclohexane (■) ($r^2 = 0.986$) as reference compounds at 298 K and atmospheric pressure of air.

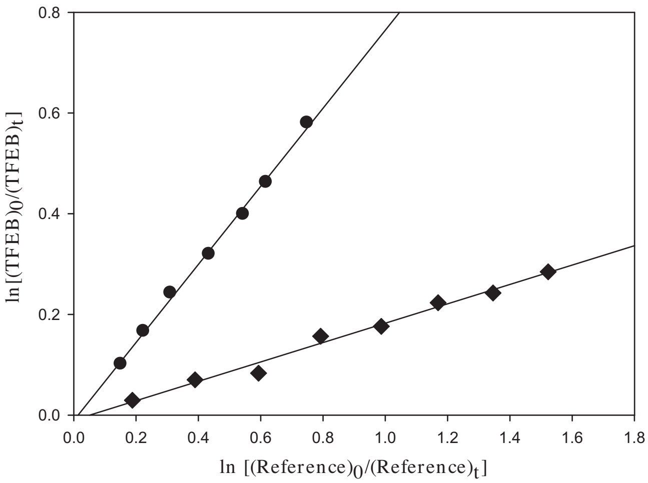


Figure 2. Relative rate data for the reaction of Cl with 2,2,2-trifluoroethyl butyrate using ethyl acetate (●)($r^2 = 0.997$) and acrylonitrile (♦) ($r^2 = 0.986$) as reference compounds at 298 K and atmospheric pressure of air.

The following averaged values of the rate coefficients have been obtained:

$$k_1 = (1.3 \pm 0.3) \times 10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$$

$$k_2 = (4.7 \pm 1.1) \times 10^{-11}\,\text{cm}^3\text{molecule}^{-1}\,\text{s}^{-1}$$

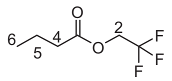
The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have considered also the corresponding error on the reference rate coefficients ((5)–(8)).

5. Discussion

To the best of our knowledge, no kinetic data of the reactions of OH radicals and Cl atoms with 2,2,2-trifluoroethyl butyrate have been reported previously. The present study, thus, is the first measurement of the rate coefficients of the reactions (1) and (2) and therefore no direct comparison with the literature can be made.

Rate coefficient for the reaction of OH with TFEB has been estimated using the US EPA AOPWIN program [13] which is based upon the structure-activity relationship (SAR) method described in Kwok and Atkinson [14]. The estimated OH rate coefficient by this method was 1.778×10^{-12} cm^3 molecule^{-1} s^{-1}. The SAR rate coefficient prediction for this reaction is in good agreement with the value of $(1.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} determined in this study.

It is estimated that the fractions of the overall OH radical reaction proceeding by H-abstraction from the C-H bonds at the 2 (C(O)OCH$_2$–), 4 (–CH$_2$–C(O)O), 5 (–CH$_2$–) and 6 (CH$_3$–) positions are (in cm^3 molecule^{-1} s^{-1}) 0.106×10^{-12}, 0.356×10^{-12}, 1.149×10^{-12} and 0.167×10^{-12}, respectively.



The rate coefficients for hydrogen abstraction from (C(O)OCH$_2$–), (–CH$_2$-C(O)O–), (–CH$_2$–) and (CH$_3$–) groups depend on the identity

Table 1
Reference compound, measured rate coefficient ratios, $k_{TFEB}/k_{reference}$, and the obtained rate coefficients for the reactions of OH radicals and Cl atoms with 2,2,2-trifluorethyl butyrate at 298 K in 760 Torr of air.

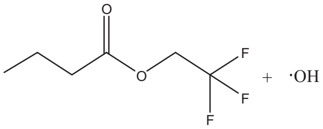
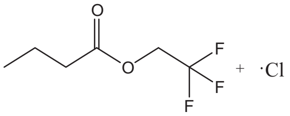
Reaction	Reference	$k_{TFEB}/k_{reference}$	k_{TFEB} cm^3 molecule^{-1} s^{-1}
	Ethyl acetate	0.78 ± 0.02	$(1.4 \pm 0.2) \times 10^{-12}$
	Ethyl acetate	0.78 ± 0.05	$(1.4 \pm 0.2) \times 10^{-12}$
	Cyclohexane	0.21 ± 0.02	$(1.3 \pm 0.3) \times 10^{-12}$
	Cyclohexane	0.19 ± 0.01	$(1.2 \pm 0.2) \times 10^{-12}$
		Average	$(1.3 \pm 0.3) \times 10^{-12}$
	Ethyl acetate	2.58 ± 0.10	$(4.5 \pm 0.9) \times 10^{-11}$
	Ethyl acetate	2.73 ± 0.16	$(4.8 \pm 1.0) \times 10^{-11}$
	Acrylonitrile	0.45 ± 0.01	$(4.9 \pm 1.1) \times 10^{-11}$
	Acrylonitrile	0.42 ± 0.01	$(4.7 \pm 1.1) \times 10^{-11}$
		Average	$(4.7 \pm 1.1) \times 10^{-11}$

Table 2
Comparison of the rate coefficient values for the reaction of OH radicals and Cl atoms with a series of fluoroacetates including TFEB at 298 K.

Fluoroacetate	k_{OH} (cm^3 molecule^{-1} s^{-1})	$k_{Cl} \times 10^{10}$ (cm^3 molecule^{-1} s^{-1})
$CF_3C(O)OCH_3$	4.97×10^{-14} [a]	9.00×10^{-14} [c]
$CF_3C(O)OCH_2CH_3$	2.64×10^{-13} [a]	1.79×10^{-12} [c]
$CF_2HC(O)OCH_3$	1.48×10^{-13} [a]	2.03×10^{-13} [c]
$CF_3C(O)OCH_2CF_3$	1.05×10^{-13} [a]	1.18×10^{-15} [c]
$CH_3CH_2CH_2C(O)OCH_2CF_3$	1.30×10^{-12} [b]	4.70×10^{-11} [b]

[a] From reference [5].
[b] This Letter.
[c] From Reference [6].

of the substituents attached to these groups. These rate coefficients estimated, and as intuitively one would expect, suggest that the main H-abstraction (around 65%) will be in the position 5 (–CH_2–) due to electron-donating alkyl groups substituents like –CH_3 and –CH_2– groups. The lower H-abstraction (around 6%) will be in the position 2 (–C(O)O–CH_2–CF_3) consistent with an increase of the negative inductive effect from –CF_3 group.

This inductive effect of fluorinated groups is observed if we compare the OH rate coefficient of 2,2,2-trifluoroethyl butyrate with the OH rate coefficient of the corresponding fully hydrogenated ester ($CH_3CH_2CH_2C(O)OCH_2CH_3$), where $k_{CH3CH2CH2C(O)OCH2CH3} = 4.37 \times 10^{-12}$cm^3 molecule^{-1} s^{-1} [15]>$k_{CH3CH2CH2C(O)OCH2CF3} = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this work). The same tendency is observed for fluoroacetates where an increase in the substitution of H atoms by F atoms in esters overcomes the activating effect of the ester function in reactions with OH radicals leading to a reduction of the reactivity:

$k_{CH3COOCH3}$ (3.5×10^{-13}[16]) > $k_{CF2HCOOCH3}$ (1.5×10^{-13}[5]) > $k_{CF3COOCH3}$ (5.0×10^{-14}[5]) and $k_{CF3COOCH2CH3}$ (2.6×10^{-13}[5]) > $k_{CF3COOCH2CF3}$ (1.1×10^{-13}[5]) in units of cm^3 molecule^{-1} s^{-1}.

In our previous work [5,6], we reported the rate coefficients for the reactions of OH radicals and Cl atoms with a series of fluorinated esters. Table 2, lists the rate coefficient of these reactions in comparison with the kinetic results obtained in this work for TFEB. We observed from Table 2, that the rate constant of OH with TFEB is at least one order of magnitude higher than the rate coefficients of the others short chain fluoroesters. Blanco et al. [5] found that, in general, the ester linkage, –C(O)O–, activates the neighboring C–H bonds, since the reaction rates for the esters are higher than those of the corresponding halocarbons. Even though, the reactions of OH radicals with alkanes and esters proceed via a similar H-abstraction reaction [17], it has been suggested that the reactions of OH with esters also involve hydrogen-bonded complexes [18] rather than a direct H-atom abstraction pathway. Hence, the deactivating inductive effect of the carbonyl group in the esters is offset by the stabilizing effect of the hydrogen bonding. In contrast, such stabilization of the transition state by hydrogen bonding should be not possible in the reaction of TFEB with OH radicals due to the presence of a –CH_2– group between the H-atom of the attacking OH radical and the O atom of the carbonyl group, if the H-abstraction is produced in the position 5 (–CH_2–) as we explained above. In this case, the reactivity of the –C(O)OR groups in the ester should be lower than the reactivity of the corresponding alkyl (R) group in the alkane.

Unfortunately, no comparison with kinetic experimental data can be made for TFEB since the rate coefficient for reaction of OH with the analogous alkane, (1-trifluoro pentane, $CH_3CH_2CH_2CH_2CF_3$), is not available. However, it can be used the SAR method described by Kwok and Atkinson [14] to estimate the k value of the reaction of 1-trifluoropentane with OH. A calculated value of k is 2.81×10^{-12} cm^3 molecule^{-1} s^{-1} is obtained, which is 1.6 times faster than SAR estimation of 1.778×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction of OH + TFEB, supporting the above reactivity considerations.

Additionally, the rate coefficient of the reaction of Cl atoms with TFEB $(4.7 \pm 1.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is higher than the rate coefficients obtained in our previous work for the reactions of Cl with similar fluoroacetates (see Table 2). We can explain this difference thinking that the main H-abstraction will be in the position 5 (–CH_2–) which is favored by the electron-donating alkyl groups substituents like –CH_3 and –CH_2–groups which is not observed in the case of fluoroacetates listed in Table 2. No kinetic data for the reaction of the corresponding fluoroalkane (1-trifluoro pentane) with Cl atoms is available in the literature but we expect that the rate coefficient of the haloalkane will be faster than the rate constant of TFEB with Cl atoms, since, the stabilization of the transition state by hydrogen bonding is not possible in this reaction.

The rate coefficients obtained in this work and the rate coefficients for the reactions of the fluoroacetates with OH and Cl obtained in previous work are listed in Table 2. These OH and Cl rate coefficients were incorporated in our previous reported correlation between k_{OH} *vs.* k_{Cl} for a series of halogenated organic compounds for which the same H-abstraction mechanism is operative [19].The correlation obtained in our previous study for a number of different compounds (chloroalkanes, fluoroalkanes, chlorofluoroalkanes, fluoroethers, chloroethers, chlorofluoroethers and chlorofluoroesters) was described as follows [17]:

$$\log k_{OH} = 0.485 \log k_{Cl} - 7.00 \tag{II}$$

We have added in this plot the experimental values of k_{OH} *vs.* k_{Cl} for the reactions of OH and Cl with the series of fluoracetates obtained

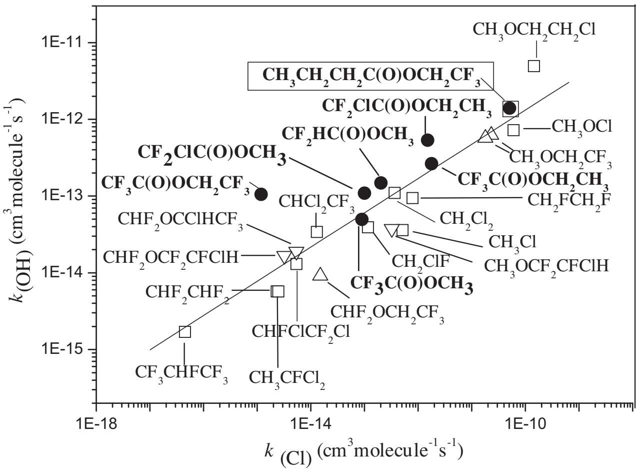


Figure 3. Plot of log k_{OH} *vs.* log k_{Cl} ($r^2 = 0.89$): (○) chloroalkanes, fluoroalkanes and chlorofluoroalkanes [20], (△) fluoroethers [20], (□) chloroethers [20], (▽) chlorofluoroethers [20] and (●) chlorofluoroesters [19], fluoroesters [5,6] and TFEB (this Letter).

previously [5,6] and listed in Table 2 together with the rate coefficients obtained in this work for the reaction of TFEB with OH and Cl obtaining the new correlation plotted in Figure 3. A least-squares treatment of the data points in Figure 3 yields now the following updated expression:

$$\log k_{OH} = 0.447 \log k_{Cl} - 7.41 \qquad \text{(III)}$$

with the rate coefficients in units of cm^3 molecule^{-1} s^{-1}. The good quality of the correlation between the reaction rate coefficients of OH radicals and Cl atoms is such that it can be used to estimate rate coefficients of reactions which have not yet been investigated.

5.1. Implications for atmospheric chemistry

Regarding 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 2,2,2-trifluoroethyl butyrate due to reaction with OH radicals and Cl atoms. Unfortunately, no kinetic data are available for the reaction of TFEB with NO_3 radicals or O_3 molecules. Nevertheless, reactions of saturated esters with O_3 or NO_3 radicals are expected to be of negligible importance [21]. The atmospheric lifetimes can be calculated using the expression: $\tau_x = 1/k_x[X]$ with X = OH or Cl, where k_x is the rate coefficient for the reaction of the oxidant X with the TFEB and [X] is the typical atmospheric concentration of the oxidant, as follows:

Ester	τ_{OH}	τ_{Cl}
2,2,2-Trifluoroethyl butyrate	4 days	24 days

In these calculations the following rate constant values were used: $k_{OH} = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this Letter), $k_{Cl} = 4.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this Letter).

Typical oxidant concentrations in the atmosphere have been used: $[OH] = 2 \times 10^6$ radicals cm^{-3} [22] and $[Cl] = 1 \times 10^4$ atoms cm^{-3} [23].

The atmospheric lifetimes obtained for TFEB, in the order of few days, are considerably shorter than for other fluorinated small chain esters as fluoroacetates (between months and years) by its reactions with OH radicals or Cl atoms [5,6].

The low Henry's law coefficients of esters, $K_H < 10$ M atm^{-1} at 298 K [24], probably preclude wet deposition from being a significant atmospheric loss mechanism. Kutsuna et al. [24] have suggested that dissolution in clouds serves only a minor atmospheric sink for some fluoroesters, although its dissolution in ocean water could be significant. The volatility of these compounds will render dry deposition and unlikely removal mechanism. Photolytic loss of the haloesters will be negligible since they are photolytically stable in the actinic region of the electromagnetic spectrum [19].

In conclusion, the atmospheric lifetime is determined by the OH-initiated oxidation for TFEB. Although, in the early morning hours in marine environments, Cl-atom initiated reactions could compete with the OH reaction [6].

This species survives long enough to become well dispersed from the source origin in which regional scale transport is likely. Urban emissions of this compound are, therefore, unlikely to contribute to local ozone and photooxidant formation.

The OH radical initiated atmospheric degradation of the studied TFEB is expected to result in the formation of mainly acids, aldehydes and dicarbonyls compounds which will be subject to further reaction with OH and also photolysis. In particular, acids with lower molecular weight are highly soluble compounds and may be rapidly incorporated into cloud droplets, contributing to the acidity of precipitation [7,8].

Further experiments, to study the product distribution of different fluoroesters reactions would be desirable to obtain a better understanding of the atmospheric implications associated with the widespread use of fluoroethers on air quality and their contribution to the acid precipitation in general.

Acknowledgments

The authors wish to acknowledge the CONICET (Argentina), ANPCyT-FONCYT (Argentina), SECyT-UNC (Córdoba, Argentina), CONACyT (Paraguay), AUGM and PRI-UNC (Argentina) for financial support of this research.

References

[1] M.J. Molina, F.S. Rowland, Nature 249 (1974) 810.
[2] A. Sekiya, S. Misuki, J. Fluor. Chem. 101 (2000) 215.
[3] J.G. Calvert, A. Mellouli, J.J. Orlando, M.J. Pilling, T.J. Wallington, The Mechanism of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, 2011.
[4] L. Chen, T. Uchimaru, S. Kutsuna, A. Sekiya, J. Thromb. Res. 514 (2011) 207.
[5] M.B. Blanco, M.A. Teruel, Atmos. Environ. 41 (2007) 7330.
[6] M.B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M.A. Teruel, Chem. Phys. Lett. 453 (2008) 18.
[7] M.B. Blanco, I. Bejan, I. Barnes, P. Wiesen, M.A. Teruel, Environ. Sci. Technol. 44 (2010) 2354.
[8] M.B. Blanco, I. Barnes, M.A. Teruel, J. Phys. Org. Chem. 23 (2010) 950.
[9] B. Picquet et al., Int. J. Chem. Kinet. 30 (1998) 839.
[10] E.W. Wilson, W.A. Hamilton, H.R. Kennington, B. Evans, N.W. Scott, W.B. DeMore, J. Phys. Chem. A 110 (2006) 3593.
[11] J.H. Xing, K. Takahashi, M.D. Hurley, T.J. Wallington, Chem. Phys. Lett. 474 (2009) 268.
[12] M.A. Teruel, M.B. Blanco, G.R. Luque, Atmos. Environ. 41 (2007) 5769.
[13] W.M. Meylan, P.H. Howard, Chemosphere 26 (1993) 2293. Available from: <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>.
[14] E.C. Kwok, R. Atkinson, Atmos. Environ. 29 (1995) 1685.
[15] C. Ferrari, A. Roche, V. Jacob, P. Foster, P. Baussand, Int. J. Chem. Kinet. 28 (1996) 609.
[16] A. El Boudali, S. Le Calve, G. Le Bras, A. Mellouki, J. Phys. Chem. 100 (1996) 12364.
[17] K.G. Kambanis, Y.G. Lazarou, P. Papagiannakopoulos, J. Phys. Chem. A 102 (1998) 8620.
[18] I.W.M. Smith, A.R. Ravishankara, J. Phys. Chem. A 106 (2002) 4798.
[19] M.B. Blanco, M.A. Teruel, Chem. Phys. Lett. 441 (2007) 1.
[20] http://kinetics.nist.gov/kinetics/index.jsp.
[21] C.W. Spicer et al., Nature 394 (1998) 353.
[22] R. Hein, P.J. Crutzen, M. Heimann, Global Biogeochem. Cycles 11 (1997) 43.
[23] O.W. Wingenter, M.K. Kubo, N.J. Blake, T.W. Smith, D.R. Blake, F.S. Rowland, J. Geophys. Res. 101 (1996) 4331.
[24] S. Kutsuna, L. Chen, K. Ohno, K. Tokuhashi, A. Sekiya, Atmos. Environ. 38 (2004) 725.