Relative rate coefficients of OH radical reactions with $CF_3CF=CClCF_3$ and $CF_3CH=CHCH_2OH$. Ozone depletion potential estimate for $CF_3CF=CClCF_3$

Juan Pablo Aranguren Abrate [a], Ignacio Pisso [b], Silvina Anahí Peirone [a], Pablo Marcelo Cometto [a], Silvia Irene Lane [a,*]
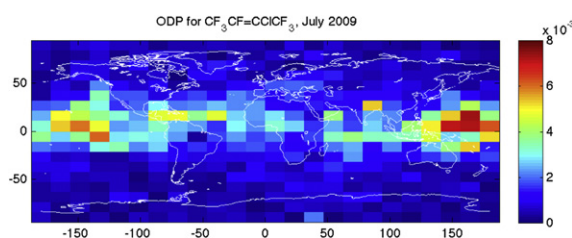
[a] Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Centro de Laser de Ciencias Moleculares, Universidad Nacional de Córdoba, Ciudad Universitaria, Pabellón Argentina, Ala 1, 5000 Córdoba, Argentina
[b] Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, 3173-25 Showa-machi, Kanazawa-ku, Yokohama-city, Kanagawa 236-0001, Japan

HIGHLIGHTS

- ► Reaction rate constants for OH with $CF_3CF=CClCF_3$ and $CF_3CH=CHCH_2OH$ were determined.
- ► Atmospheric lifetimes of $CF_3CF=CClCF_3$ and $CF_3CH=CHCH_2OH$ were estimated.
- ► ODP calculations for $CF_3CF=CClCF_3$ were performed.
- ► ODP of $CF_3CF=CClCF_3$ depends on emission scenarios.
- ► ODP of $CF_3CF=CClCF_3$ is of minor importance, but not zero.

GRAPHICAL ABSTRACT

ODP for $CF_3CF=CClCF_3$, July 2009

ABSTRACT

The relative rate method was used to determine the rate coefficients for the reactions of OH radicals with $CF_3CF=CClCF_3$ (k_1) and $CF_3CH=CHCH_2OH$ (k_2). Experiments were carried out at (298 ± 2) K and atmospheric pressure using ultra pure air or ultra pure nitrogen as the gas bath. The k_1 value was measured relative to those of chloroethane and ethane, and the k_2 value was measured relative to those of cyclohexene and 1-pentene. The following rate coefficients were derived in units of cm^3 molecule^{-1} s^{-1}: $k_1 = (3.3 \pm 0.9) \times 10^{-13}$ and $k_2 = (3.3 \pm 0.9) \times 10^{-11}$. This is the first experimental determination of k_1 and k_2. The rate coefficients were used to estimate the atmospheric lifetimes for the studied haloalkenes considering the OH-initiated oxidation process. The ozone depletion potential (ODP) for $CF_3CF=CClCF_3$ was estimated following a recently-developed technique based on Lagrangian trajectories, which takes into account the time and location of the release of the short-lived halogenated species.

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1. Introduction

Halocarbons have been used as refrigerants, blowing agents, cleaning fluids, solvents, and as fire-extinguishing agents. They have been shown to cause stratospheric ozone depletion and have been banned for many uses (Tapscott et al., 2000). Perhaloalkenes are used to synthesize fluoropolymers that, due to their excellent barrier properties, chemical and physical inertness, and hydrophobic character, are extensively exploited for applications such as moisture and noxious gas barriers, anticorrosion and non-stick coatings. Moreover, fluorinated alkenes are the most likely reactive impurities in hydrochlorofluorocarbons (HCFCs), either as residual starting materials from production or as decomposition products (Orkin et al., 1997). The $CF_3CF=CClCF_3$ has been recently

proposed as a foam blowing agent based partially on the fact that this compound supposedly, presents a low or near-zero ODP (Singh et al., 2009). However the ODP value of this compound has not yet been estimated.

Hydrofluorocarbons (HFCs) have been suggested as potential substitutes of chlorofluorocarbons (CFCs) because they do not contain chlorine atoms and therefore make no contribution to the stratospheric ozone destruction (Wallington et al., 1995). Fluorinated alcohols are used as cleaning agents (Fluorocarbon Manufacturers Association, 1990) as well as in a variety of industrial applications (Hurley et al., 2005). In particular, $CF_3CH=CHCH_2OH$ has been proposed for pharmaceutical formulations to obtain improved aerosol drug suspension characteristics, i.e. by increasing phase separation times and producing a finer suspension (Rogueda, 2006).

Scant kinetic data exist for the reactions of halogenated alkenes (HA) containing the $-CF_3$ group in a vinyl position with atmospheric oxidants. There are only a few available values of the rate coefficients for reactions with the OH radical. These reactions are with $CF_3CH=CH_2$ (Orkin et al., 1997; Sulbaek Andersen et al., 2005), $CF_3CF=CH_2$ (Orkin et al., 1997, 2010; Papadimitriou et al., 2008; Nielsen et al., 2007), $(Z) - CF_3CF=CHF$ (Orkin et al., 2010; Hurley et al., 2007), $(E) - CF_3CF=CHF$ (Hurley et al., 2007), $(Z) - CF_3CH=CHF$ (Nilsson et al., 2009), $(E) - CF_3CH=CHF$ (Orkin et al., 2010; Søndergaard et al., 2007), $(E) - CF_3CH=CHCl$ (Sulbaek Andersen et al., 2008), $CF_3CF=CF_2$ (Orkin et al., 1997; Tokuhashi et al., 2000; Mc Ilroy and Tully, 1993; Mashino et al., 2000; Acerboni et al., 2001), $CF_3CCl=CCl_2$ (Cometto et al., 2010), (Z/E) $CF_3CF=CFCF_3$ (Young et al., 2009; Tokuhashi et al., 2001; Orkin et al., 2011), $(Z) - CF_3CF=CFCF_3$ (Orkin et al., 2011), $(E) - CF_3CF=CFCF_3$ (Orkin et al., 2011), $(CF_3)_2C=CFC_2F_5$ (Orkin et al., 2011) and $(Z/E) - CF_3CCl=CClCF_3$ (Cometto et al., 2010).

We report here an experimental study of the kinetics of the following reactions:

$$OH + (Z/E) - CF_3CF=CClCF_3 \rightarrow Products \quad (k_1) \qquad (1)$$

$$OH + (Z/E) - CF_3CH=CHCH_2OH \rightarrow Products (k_2) \qquad (2)$$
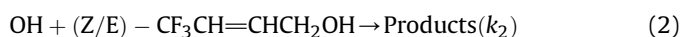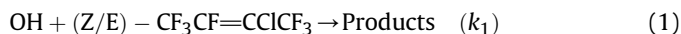
We have used a relative rate method to obtain the second-order rate coefficients (k_1 and k_2) at 298 K and atmospheric pressure. To the best of our knowledge, this is the first experimental determination of the rate coefficients at 298 K for both reactions.

The present work aims to extend the existing scant database of rate coefficients for the reactions of OH radicals with halogenated alkenes. In addition haloalkenes are used in industrial applications,

therefore information on their atmospheric chemistry and environmental impact is needed. Hence, the atmospheric implications of reactions 1 and 2 have been investigated, calculating the atmospheric lifetimes for $(Z/E) - CF_3CF=CClCF_3$ and $(Z/E) - CF_3CH=CHCH_2OH$ and estimating the ozone depletion potential (ODP) for $(Z/E) - CF_3CF=CClCF_3$.

2. Experimental

2.1. Kinetic measurements

All experiments were carried out in a 200 L collapsible Teflon bag at (298 ± 2) K and atmospheric pressure (750 ± 10 Torr). Reaction mixtures consisting of a reference organic compound and the sample organic reactant diluted in ultra pure N_2 or ultra pure air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. A conventional greaseless vacuum system was used for all the experiments. Pressure measurements were performed with a capacitance manometer, MKS 220A. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of ultra pure N_2 or ultra pure air and the bag was then filled to its full capacity at atmospheric pressure.

Before each set of experiments the Teflon bag was cleaned by filling it with a mixture of O_2 and N_2 which was irradiated for 15–40 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 checked by gas chromatography that there were no observable impurities, before performing the experiments.

The initial concentration of $(Z/E) - CF_3CF=CClCF_3$ and $(Z/E) - CF_3CH=CHCH_2OH$, the compound used as reference in each independent experiment and its corresponding initial concentration in the chamber are shown in the Table 1. The H_2O_2 concentrations used were in the range 170–220 ppm, and it was introduced into the chamber by a Hamilton syringe through a stream of ultra pure N_2 or ultra pure air.

The Teflon bag was surrounded by six germicide lamps (Philips 30 W), providing UV radiation with a λ maximum around 254 nm. In the present work, typically between 4 and 6 of these lamps were used to produce OH radicals by the UV photolysis of H_2O_2 and the time of photolysis varied from 1 to 25 min and 0.5–7 min for reactions 1 and 2, respectively.

Periodically, gas samples were removed from the Teflon bag using calibrated gas syringes. The organics were monitored by gas chromatography (Perkin Elmer Clarus 500) coupled with flame

Table 1
Initial concentration of the reactants, rate coefficient ratios, k_{HA}/k_{Ref}, and the absolute rate coefficients, k_{HA}, for the reactions of OH radicals with the studied halogenated alkenes (HA) at 298 K and atmospheric pressure.

HA	$[HA]/_0$ppm	Reference	$[Ref]/_0$ppm	Run	k_{HA}/k_{Ref}	$k_{HA}/10^{-12}$ (cm^3 molecule^{-1} s^{-1})
$(Z/E) - CF_3CCl=CFCF_3$	31	Chloroethane	52	1	(0.83 ± 0.02)	(0.31 ± 0.06)
	70		39	2	(0.93 ± 0.02)	(0.34 ± 0.06)
	61	Ethane	96	1	(1.50 ± 0.03)	(0.35 ± 0.07)
	105		66	2	(1.28 ± 0.03)	(0.31 ± 0.06)
	59		102	3[a]	(1.32 ± 0.02)	(0.32 ± 0.06)
Average						(0.33 ± 0.09)
$(Z/E) - CF_3CH=CHCH_2OH$	52	Cyclohexene	31	1	(0.47 ± 0.01)	(32 ± 7)
	153		96	2	(0.48 ± 0.03)	(32 ± 8)
	57		92	3	(0.48 ± 0.02)	(32 ± 8)
	66	1-pentene	39	1	(1.12 ± 0.03)	(36 ± 2)
	31		61	2	(1.03 ± 0.04)	(33 ± 3)
	77		102	3[a]	(1.08 ± 0.04)	(34 ± 3)
Average						(33 ± 9)

[a] Experiments carried out with ultra pure air as gas bath.

ionization detection (FID), using Elite-264 (30 m × 0.32 mm × 0.25 μm) and Elite-5MS (30 m × 0.32 mm × 0.25 μm) capillary columns for $(Z/E) - CF_3CF=CClCF_3$ and $(Z/E) - CF_3CH=CHCH_2OH$ studies, respectively. The chromatographic runs were isothermal and ultra pure He was used as carrier gas.

2.2. Materials

The chemicals used were N_2 (Linde 99.999%. CAS: 7727-37-9), O_2 (Linde 99.999%. CAS: 7782-44-7), He (Linde 99.999%. CAS: 7440-59-7), ultra pure air (synthetic air SS Linde), $(Z/E) - CF_3CF=CClF_3$ (Apollo Scientific 99%. CAS: 437-41-3), $(Z/E) - CF_3CH=CHCH_2OH$ (Apollo Scientific 99%. CAS: 674-53-3). H_2O_2 (70.5%. CAS: 7722-84-1) was supplied by Atanor S.A, ethane (≥99%. CAS: 74-84-0), chloroethane (≥98%. CAS: 75-00-3), cyclohexene (99%. CAS: 110-83-8) and 1-pentene (≥98.5%. CAS: 109-67-1) were supplied by Sigma Aldrich. The organics were degassed by repeated freeze–pump–thaw cycling and purified by vacuum distillation until gas chromatographic analysis revealed no observable impurities.

3. ODP calculations

The ODP of $(Z/E) - CF_3CF=CClCF_3$ as a function of the time and location of emission is the ratio of the total ozone depleted by a mass amount of this compound relative to the total ozone depleted by the same mass amount of $CFCl_3$ (CFC-11) released into the atmosphere at the same location and time. For long-lived species, the ODP value depends weakly on the time and location of release; whereas, for species with tropospheric mean lifetime shorter than the time scale of transport into the stratosphere (of the order of 6 months), the proportion of mass being loaded into the stratosphere depends on its tropospheric lifetime.

The method used in this work for the estimation of the total stratospheric ozone depleted is based on full 3D trajectory calculations and a simplified chemical scheme that has been extensively described elsewhere (Pisso et al., 2010). The trajectory-based method was developed specifically for very short-lived species (VSLSs), and Lagrangian calculations provide a detailed description of transport, both in the troposphere and in the stratosphere, yielding estimates of total depleted stratospheric ozone for both VSLS and CFC-11. Two separate ensembles of trajectory calculations, for the stratosphere and the troposphere respectively, are needed to estimate the ODP according to its definition.

The stratospheric ozone depletion occurs as long as the reactive chlorine injected across the tropopause remains in the stratosphere. The stratospheric residence time of an air mass depends on the location within the tropopause where the injection occurs, e.g. longer residence times are associated with lower latitudes. The ozone depletion occurs regardless of the source of active chlorine is the VSLS or the CFC-11. Hence the total overall depletion caused by the short lived chlorinated species released at the tropopause is proportional to the total injection of source and product gas respect to the total amount of CFC-11 injected at the same point. However, if the release occurs at the surface, while the CFC-11 injected is proportional to the total air injected because of the absence of tropospheric reactions, the amount of VSLS injected into the stratosphere depends of the path from the surface to the tropopause and on the decay and rainout processes along this path.

To estimate the decay and rainout along the path in the troposphere, a large ensemble (>2500000 trajectories) is initialized within the planetary boundary layer across the surface of the globe and run forward for 6 months. A control region for injection into the stratosphere is defined (here the layer between 380 K and 400 K) and for every trajectory the time of injection after release is recorded. As the air mass travels across the troposphere, the insoluble source gas is transformed (photolized/oxydized) into soluble product gases which are in turn rained out and hence the fraction of the emitted VSLS reaching the control surface can be estimated for every individual trajectory of the larger ensemble. The key parameter for this step of the calculation is precisely the mean tropospheric lifetime studied experimentally in this work. This enables a posteriori (i.e. offline after the trajectories have been stored) clustering trajectories by emission regions (e.g. Lat-Lon grids at the PBL) allowing to estimate for every emission region the transfer function into the stratosphere. This means to estimate the probability of a molecule emitted at that time and location at the surface to be injected into the stratosphere across a certain location at a certain time (e.g. Lat-Lon grid at the 'tropopause') taking into account the decay and rainout processes. After the air mass has entered into the stratosphere the scavenging of product gas ceases and it can be safely assumed that the injected chlorine is capable of deplete ozone until ejected back into the troposphere.

In the general case for an unspecified halogenated species, both the stratospheric and tropospheric calculations are combined in order to estimate the total ozone depleted by an individual pollutant release. Every individual event of injection across a certain position and a certain time into the stratosphere associated with the original release at the surface has to be weighted with the expected stratospheric residence time at the tropopause (calculated with stratospheric trajectories as explained above).

In the present work a new computational modeling work was performed respect to (Pisso et al., 2010) where the method has first introduced. Two trajectories ensembles corresponding to January and July of 2009 were released and calculated for six months. The simplified chemistry along the trajectories represented by the mean tropospheric lifetime has been updated to make it consistent with the experimental tropospheric mean lifetimes derived from kinetic measurements. This is the first time that such calculations have been performed on purpose for a newly estimated reaction rates.

Uncertainties of the ODP calculation method are associated with tropospheric chemistry and transport (in the present method the products of the reaction 1 are considered to be rapidly removed by washout), but also with the representation of stratospheric chemistry (ozone depletion by heterogeneous reactions) and transport (large scale stratospheric circulation) required to represent the depletion caused by long-lived CFC-11. In this study the species considered involve chlorine only, therefore reducing uncertainties associated with stratospheric processes modeling.

Additionally, for comparison purposes, a global ODP value was also calculated with the semi-empirical method developed by Solomon and Albritton (1992), using the following equation:

$$ODP_x(t) = \left\{ \frac{F_x}{F_{CFC-11}} \right\} \frac{M_{CFC-11}}{M_x} \frac{n_x}{3} \alpha \frac{\int_{t_s}^{t} \exp(-(t-t_s)/\tau_x)dt}{\int_{t_s}^{t} \exp(-(t-t_s)/\tau_{CFC-11})dt}$$

(3)

The term in brackets $\{F_x/F_{CFC-11}\}$ is the fraction of the compound x ($CF_3CF=CClCF_3$ in our case) that has been dissociated in the stratosphere compared to that of CFC-11, determined from atmospheric measurements. M denotes the molecular weight, n_x is the number of chlorine, bromine or iodine atoms in X, and α is an enhancement factor that reflects the relative efficiency of ozone destruction by bromine or iodine. The time t_s is the time for a molecule to be transported from the terrestrial surface to the

stratosphere, and t is the total time. τ_X and τ_{CFC-11} are the lifetimes of X and CFC-11. It has to be recalled that this simplified formula was originally derived for long lived gases and it is is not well suited for VSLSs species. This was the reason why a new methodology was developed (Pisso et al., 2010).

4. Results and discussion

4.1. Kinetic measurements

The rate coefficients for the reactions 1 and 2 were determined relative to the rate coefficient for the reaction of OH with the reference compounds:

$$OH + haloalkene \rightarrow Products(k_{HA}) \tag{4}$$

$$OH + reference \rightarrow Products(k_{Ref}) \tag{5}$$
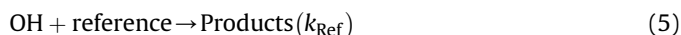
Provided that the reactant and the reference compound are lost only by reactions 4 and 5, respectively, then it can be shown that

$$\ln\left(\frac{[HA]_0}{[HA]_t}\right) = \frac{k_{HA}}{k_{Ref}}\ln\left(\frac{[Ref]_0}{[Ref]_t}\right) \tag{6}$$

where $[HA]_0$, $[Ref]_0$, $[HA]_t$ and $[Ref]_t$ are the concentrations of the haloalkene and reference compound at times $t = 0$ and t, respectively and k_{HA} and k_{Ref} are the second-order rate coefficients of reactions 4 and 5, respectively.

The rate coefficients for reactions 1 and 2 were measured at (298 ± 2) K and atmospheric pressure, relative to the rate coefficients of OH with chloroethane and ethane for reaction 1 and cyclohexene and 1-pentene for reaction 2 (Table 1). The rate coefficients in units of cm^3 molecule^{-1} s^{-1} of the reaction of OH with the reference compounds used in this work were taken as $(3.7 \pm 0.6) \times 10^{-13}$ for chloroethane (Sander et al., 2011), $(2.4 \pm 0.4) \times 10^{-13}$ for ethane (Atkinson et al., 2006), $(6.74 \pm 1.35) \times 10^{-11}$ for cyclohexene (Atkinson, 1986) and $(3.19 \pm 0.14) \times 10^{-11}$ for 1-pentene (Atkinson, 1986, Atkinson and Aschman, 1984).

The relative rate method relies on the assumption that both, the haloalkene and the reference compound, are removed solely by reaction with OH radicals. To verify this assumption, mixtures of H_2O_2 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 H_2O_2, in the absence of UV light, was of negligible importance since the reagent concentrations did not change over the typical time periods used in this work. Additionally, to test for possible photolysis of the reactants used, mixtures of the reactants in N_2, in the absence of H_2O_2, were irradiated for 30 min, using the output of all the germicidal lamps surrounding the chamber. No photolysis of any of the reactants was observed.

The rate coefficients for reactions 1 and 2, k_1 and k_2, were obtained from the ratio k_{HA}/k_{Ref} as the value of k_{Ref} was known. The ratio of the rate coefficients was determined from the slopes of the plots shown in Figs. 1 and 2, and these were calculated from linear least-squares analysis of the experimental data using the Eq. (6). For each haloalkene (HA) studied, two reference compounds were used for the rate coefficient determination and, at least, two runs were performed with the same reference compound.

Figs. 1 and 2 show typical plots of ln([HA]$_0$/[HA]$_t$) vs. ln([Ref]$_0$/[Ref]$_t$), obtained for reaction 1 using chloroethane and ethane as reference compounds and for reaction 2, using cyclohexene and 1-pentene as reference compounds. The linearity of the data points, with correlation coefficients >0.99, along with the facts that: i) the
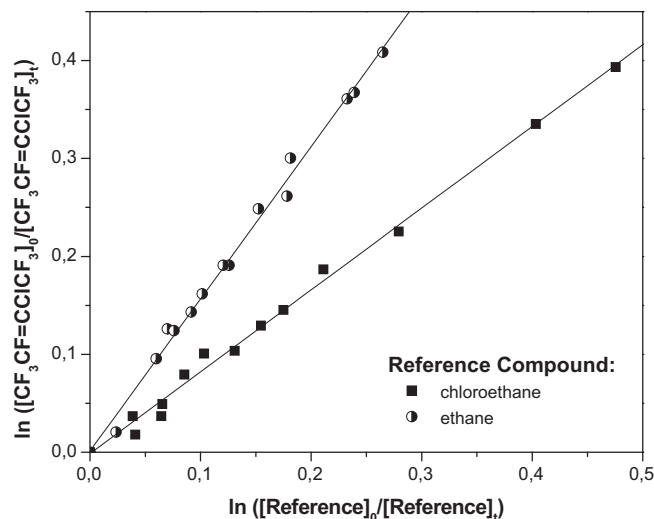

Fig. 1. Typical plots of ln ([CF$_3$CF=CClCF$_3$]$_0$/[CF$_3$CF=CClCF$_3$]$_t$) vs. ln ([Reference]$_0$/[Reference]$_t$) of the relative rate coefficients determination for the reaction of OH with CF$_3$CF=CClCF$_3$ using two different reference compounds at 298 K and 750 Torr.

plots show practically zero intercepts, ii) no noticeable differences in the obtained rate coefficients were observed using different reference compounds in the absence or presence of O_2 and varying significantly [HA]$_0$/[Ref]$_0$ ratios, and iii) the kinetic measurements were carried out at times shorter than one lifetime, suggest that the contribution of secondary reactions with the products of the reactions here studied could be considered negligible.

Table 1 shows the reference compounds, number of runs, the obtained ratios between k_{HA} and k_{Ref} and the derived second-order rate coefficients for the OH reaction with the two haloalkenes studied.

The obtained values for k_1 using chloroethane and ethane as reference compounds were $(3.3 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $(3.3 \pm 0.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. The obtained values for k_2 using cyclohexene and 1-pentene as reference compounds were $(3.2 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(3.4 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.
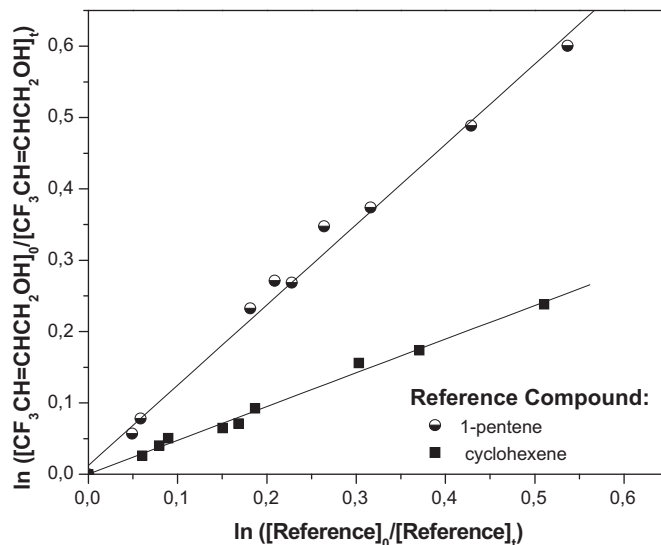
Fig. 2. Typical plots of ln ([CF$_3$CH=CHCH$_2$OH]$_0$/[CF$_3$CH=CHCH$_2$OH]$_t$) vs. ln ([Reference]$_0$/[Reference]$_t$) for the reaction of OH with CF$_3$CH=CHCH$_2$OH using two different reference compounds at 298 K and 750 Torr.

The main source of error in this method is attributed to the uncertainty associated with k_{Ref} which includes systematic errors. The experimental uncertainties are associated with the signal/noise ratio in the measurements of the chromatographic peak areas and the sampling volume uncertainty. For each individual experiment the experimental errors are quoted as twice the statistical deviation $(2\sigma_{n-1})$ stemming from the least-squares fit of the plots of $\ln([HA]_0/[HA]_t)$ vs. $\ln([Ref]_0/[Ref]_t)$ and resulted in straight lines with approximately 0 intercept ($<1\%$). The systematic uncertainties of our determinations are related to, at least, four sources: the sampling volume that is negligible compared with the total volume of the reactor, some hypothetical interference of secondary chemistry which can also be neglected due to the reasons explained above, inadequate integration method of the chromatographic areas and insufficient chromatographic resolution that, due to the careful experimental work, were minimized.

Therefore, we choose to inform values of the second-order rate coefficients that are the average of the independent experiments with a same reference compound. The errors quoted for the average values of k_1 and k_2, encompass the extremes of the individual determinations and the errors of k_1 and k_2 quoted for the individual determinations include the experimental uncertainties and the uncertainties from reference rate coefficients. We estimate in our measurements an uncertainty of 10% due to systematic errors that could be added to the final informed value of the rate coefficient.

The average second-order rate coefficients for reactions 1 and 2, considering the experiments with the different reference compounds, are:

$$k_1 = (3.3 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (3.3 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To the best of our knowledge, there are no other prior reported values of the rate coefficients for reactions 1 and 2. Thus, the present work is the first kinetic study of these reactions and, therefore, no direct comparison with the literature can be made.

4.2. Atmospheric implications: estimation of mean tropospheric lifetimes

Considering the atmospheric loss processes for the two compounds studied, their global lifetimes, τ_{global}, can be obtained from the following expression:

$$\tau_{global} = \left[\frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{other\ processes}}\right]^{-1}$$

(7)

An upper limit for the global atmospheric lifetime of the studied halogenated alkenes can be estimated by the photo-oxidation with OH radicals only. The lifetimes were calculated using the relationship $\tau_x = 1/k_x$ [OH], considering an average global concentration of OH radicals of 1×10^6 radicals cm^{-3} (global weighted-average concentration) (Prinn et al., 2001). Thus, the estimated tropospheric lifetimes are 35 days for $(Z/E) - CF_3CF=CClCF_3$ and 8 h for $(Z/E) - CF_3CH=CHCH_2OH$.

Unfortunately, no kinetic data for the reactions of $(Z/E) - CF_3CF=CClCF_3$ and $(Z/E) - CF_3CH=CHCH_2OH$ with Cl atoms, NO_3 radicals or O_3 molecules are available. However, kinetic data, available in the literature, for reactions of these species with other halogenated and perhalogenated alkenes, containing the $-CF_3$ group, suggest that the atmospheric lifetimes of these compounds, due to NO_3 and O_3 initiated photo-oxidative processes will not be important in accounting for the global lifetime (Sulbaek Andersen et al., 2005; Nielsen et al., 2007; Hurley et al., 2007; Nilson et al., 2009; Søndergaard et al., 2007; Sulbaek Andersen et al., 2008; Mashino et al., 2000; Acerboni et al., 1999, 2001; Papadimitriou et al., 2011). Moreover, from the rate coefficients available in literature (Sulbaek Andersen et al., 2005; Nielsen et al., 2007; Hurley et al., 2007; Søndergaard et al., 2007; Sulbaek Andersen et al., 2008; Mashino et al., 2000; Papadimitriou et al., 2011) the lifetimes due to depletion of alkenes containing the $-CF_3$ group by Cl atom reactions, considering a [Cl] of approximatelly 1×10^4 atoms cm^{-1} in the marine boundary layer and coastal regions (Platt et al., 2004), can reach values of 13–159 days. These values are comparable to the life time of 35 days due to OH reaction depletion for $(Z/E) - CF_3CF=CClCF_3$. Therefore, considering the similarities in the molecular structures, it is reasonable to assume that the reactions of $(Z/E) - CF_3CF=CClCF_3$ with NO_3 radicals or O_3 molecules are of minor importance, and the lifetime estimated in this work for this alkene is an upper limit due to just one relevant removal process is being considered, hence, the actual value could be lower depending on the emission scenarios.

On the other hand, the lifetimes estimated for $(Z/E) - CH_3CH=CHCH_2OH$ due to its reactions with OH, NO_3 and O_3 (Cometto et al., 2008), are comparable and these values should be treated with caution because the OH, NO_3 and O_3 concentrations vary substantially depending on environmental conditions, location and season. Therefore, taking this into account, similar considerations should be applied to $(Z/E) - CF_3CH=CHCH_2OH$, due to the similar chemical structure of this compound. Thus, we must note that the lifetime estimated in this work for this alcohol is an upper limit.

Regarding the photolytical stability of the two compounds here studied, it is reasonable to consider that tropospheric removal by photolysis is of minor importance since, from the works of Orkin et al. (1997) and Rudich et al. (1995) who obtained the UV spectra of fluorinated ethenes and propenes, and of $CH_2=CHC(CH_3)_2OH$, respectively, the absorption cross-section in the actinic region of the solar spectrum for $CF_3CF=CF_2$ and $CH_2=CHC(CH_3)_2OH$ is less than 1×10^{-22} cm^2 molecule^{-1}.

In the term "*other processes*", in Eq. (6), wet deposition is included. $(Z/E) - CF_3CF=CClCF_3$ and $(Z/E) - CF_3CH=CHCH_2OH$ have different solubility in water. $(Z/E) - CF_3CF=CClCF_3$ is sparingly soluble in water, so wet deposition for this compound is expected to be negligible, while the $(Z/E) - CF_3CH=CHCH_2OH$ is expected to be highly soluble in water (e.g., Henry's law coefficient for $CH_2=CHC(CH_3)_2OH$ is estimated around 300 M atm^{-1} at 298 K (Sander, 1999)). Therefore, the lifetime for wet deposition of $(Z/E) - CF_3CH=CHCH_2OH$ is expected to be of several months referring to calculations for fluoroalcohols (Chen et al., 2003). This lifetime is yet much longer than the lifetime toward gas-phase reactions, making negligible the loss of $(Z/E) - CF_3CH=CHCH_2OH$ by wet deposition.

As for the dry deposition, also included in the term "*other processes*", it is generally far more a local issue than the wet deposition. In the worst case, in regions with little precipitation and high concentrations of pollutants (due to industrial emissions), dry deposition is likely to be at least as important as wet deposition (World Meteorological Organization, 2011). Therefore the tropospheric removal by dry deposition, considered in Eq. (6), can be safely neglected.

4.3. Atmospheric implications: estimation of ozone depletion potentials

Taking into account the present knowledge related to the atmospheric flow and its implications of surface-to-stratosphere transport, the average tropospheric lifetime of OH provides the
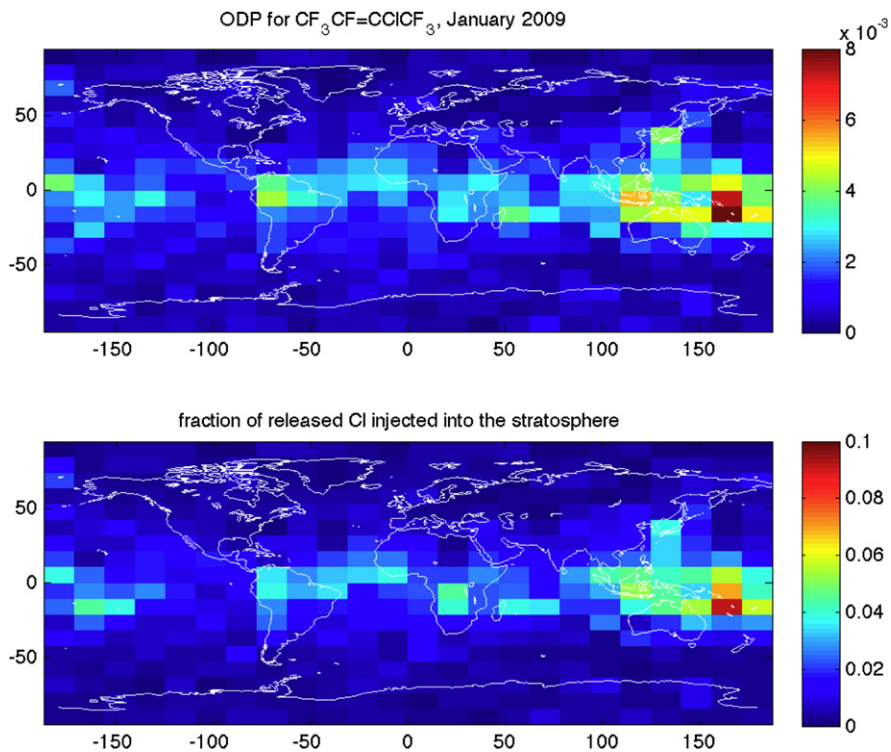
Fig. 3. ODPs and injected fractions for the source gas with a lifetime of 35 days in a 10 × 15 latitude longitude grid of the global planetary boundary layer. The calculations correspond to an ensemble of trajectories released in January 2009. Upper panel ODPs. Lower panel: injected fractions.

basis for the calculation of the ozone depletion potentials depending on the location and time of release. Fig. 3 shows the ozone depletion potentials for $(Z/E) - CF_3CF{=}CClCF_3$ and the fraction of chlorine injected across the 380 K potential temperature surface into the stratosphere depending on the release location for

January 2009 calculated using the method described in 2.1. In agreement with previous studies (Pisso et al., 2010), the ODPs are higher in the tropics with a maximum in the Western Pacific in the region known as the Warm Pool where most deep convection occurs. The distribution of the ODPs is highly inhomogeneous with
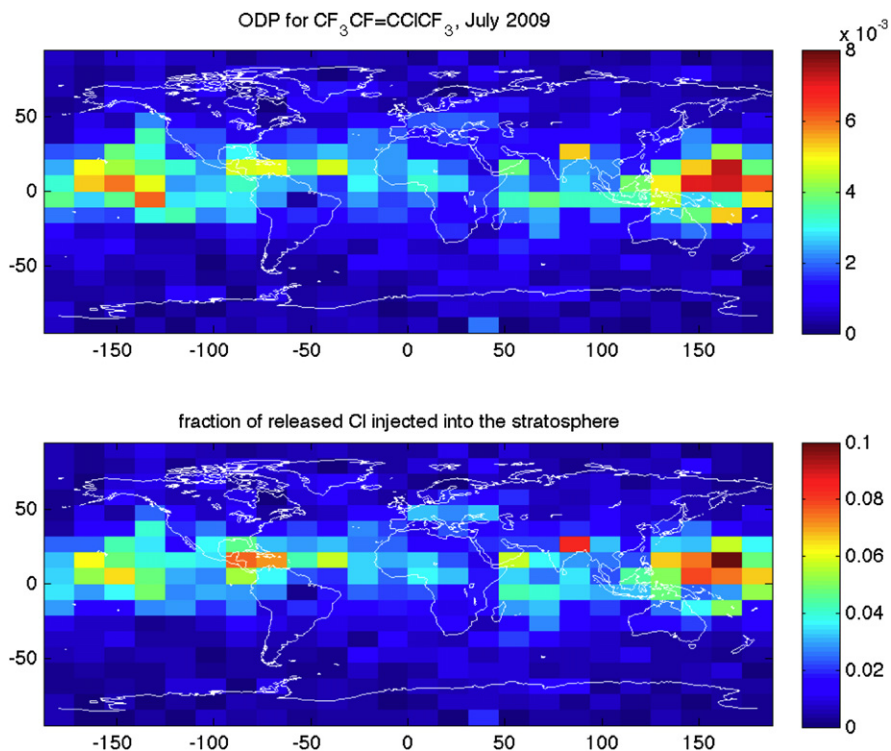

Fig. 4. ODPs and injected fractions for the source gas with a lifetime of 35 days in a 10 × 15 latitude longitude grid of the global planetary boundary layer. The calculations correspond to an ensemble of trajectories released in July 2009. Upper panel ODPs. Lower panel: injected fractions.

differences between the tropics and the polar regions reaching one order of magnitude. The injected chlorine shown in the lower panel has maximum in the warm pool in agreement with previous studies (Pisso et al., 2010 and references therein). Fig. 4 shows the ozone depletion potentials for $(Z/E) - CF_3CF=CCLCF_3$ and the fraction of chlorine injected across the 380 K potential temperature surface into the stratosphere, depending on the location of release for July 2009. The values and the patterns, both for the ODPs and the injected fractions, are consistent with the picture for January, except that the maxima are shifted towards the Northern Hemisphere following the displacement of the inter-hemispheric tropical convergence zone (ITCZ). Also, as shown in Table 2, the average values are higher than in January. This is due, in part, to the development of the Asian Monsoon and the consequent increase of troposphere-to-stratosphere transport in the monsoon anticyclone in the southern Asian region.

As mentioned before, in this method the products of the reaction 1 are considered to be rapidly removed by washout (Pisso et al., 2010). Unfortunately, no previous product studies of this reaction are available in the literature; however, taking into account the products studies carried out by Mashino et al. (2000) for the reaction of $CF_3CF=CF_2$ with OH in the presence of O_2 and NOx, we can reasonably assume that the main products for reaction 1 under atmospheric conditions are CF_3COF and CF_3COCl. The tropospheric lifetime of both products is dominated by wet deposition in clouds, with estimated values of 5 days and 6 days, respectively (George et al., 1994). A secondary pathway of the tropospheric degradation of CF_3COCl, that could become important in dry seasons, is the photolysis to give mainly CO and Cl atoms; also CF_3Cl was observed as a product with a quantum yield of 0.005. The lifetime for the photolysis process was estimated of 40–60 days (Meller et al. 1997). The formation of the fully halogenated compound CF_3Cl is crucial because it is affecting in a minor percentage, but directly, the ODP of $(Z/E) - CF_3CF=CCLCF_3$. Since the generated Cl atoms are a part of the tropospheric Cl reservoir, this would also increase, in an uncertain amount, the ODP of the studied compound. Thus, the ODP values obtained by this method should be considered as lower limits, assuming that the washout of the products, as their major sink, is in this case a very reasonable approximation.

The values of ODPs of 0.0011 and 0.0013 presented in the Table 2 as an average between 90° N and 90° S of latitude are consistent with a hypothetical global ODP value for $(Z/E) - CF_3CF=CCLCF_3$ of 0.0023, calculated also in this work with the semi-empirical method developed by Solomon and Albritton (1992), although this method was developed for long-lived species and does not describe the dependence of the ODP value with the location of the emission of a primary pollutant. It would be worthwhile to extend the comparison to other VSLSs.

We must stress that the ODP value obtained indicates that the contribution of $(Z/E) - CF_3CF=CCLCF_3$ to the depletion of stratospheric ozone is non-zero, although minor compared to CFC-11.

Table 2
Mean ODPs in January and July 2009 averaged in zonal bands corresponding to the tropics, midlatitudes and polar regions. The calculations take into account parametrized tropospheric convection.

Latitude zonal band	ODP value	
	January	July
60° N–90° N	5×10^{-4}	4×10^{-4}
30° N–60° N	7×10^{-4}	6×10^{-4}
30° S–30° N	21×10^{-4}	25×10^{-4}
30° S–60° S	6×10^{-4}	10×10^{-4}
60° S–90° S	4×10^{-4}	5×10^{-4}
90° S–90° N	11×10^{-4}	13×10^{-4}

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