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Contribution of the Atmospheric Chlorine Reactions to the Degradation of Greenhouse Gases: CFCs Substitutes

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1. Introduction

During the last few decades it has been shown that the use and dispersion of chemical compounds emitted from anthropogenic sources, firstly considered as innocuous, have dramatic effects on the global Atmosphere. The adverse environmental impacts of chlorinated hydrocarbons on the Earth's ozone layer have focused attention on the effort to replace these compounds by non-chlorinated substitutes with environmental acceptability. Although new materials have been developed for a large number of applications, a comprehensive solution remains to be found. Therefore, many provisional applications, using chemicals with unknown effects, are still currently found such as, refrigerants, foam agents, flame inhibitors, solvents, propellants, anaesthetics, etc [see for example: 3M; EPA; IPCC; Shine, 2010].

Hydrofluoroethers (HFEs) have been introduced as ozone friendly alternatives in many instances such as, refrigeration, electronic equipment, carrier fluids for lubricant deposition, and fire suppression (EPA). HFEs contain no chlorine and, thus, have ozone depletion potentials of essentially zero. One of the principal advantages of the HFE structure has been determined to be the significantly shorter atmospheric lifetimes, when compared to HFCs (hydrofluorocarbons) and PFCs (perfluorocarbons) (IPCC). However, the presence of the C-O bond, together with C-F bonds in the hydrocarbon molecule, enhance the absorption features in the atmospheric infrared window. In other words, HFEs are absorbers of infrared radiation, thus raising concern about their possible roles as greenhouse gases. Thus, it is necessary to improve our knowledge about lifetimes and global warming potentials (GWP) of these compounds in order to get a complete evaluation of their environmental impact.

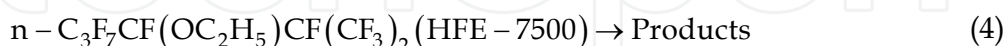
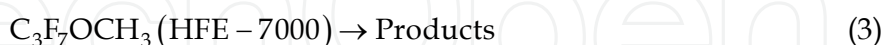
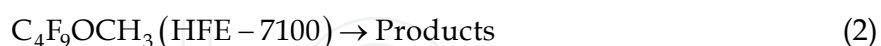
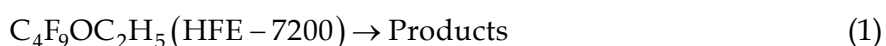
To provide an accurate evaluation of the global warming potentials, the lifetimes must first be obtained. The atmospheric lifetimes of pollutants is generally calculated on the basis of the reaction rates with OH only (Kurylo & Orkin, 2003), assuming that the reaction rates are independent of temperature. This is not suitable for chemicals with low reactivity. As a relatively homogeneous vertical distribution in the troposphere is expected, to a large extent, the losses of such chemicals take place at temperatures which are significantly lower than 298K. Thus, for reactions with relatively high activation energy, E_a , neglecting the

temperature dependence of the kinetic rate constants may lead to an underestimation of the corresponding lifetimes. In this regard, lifetimes 2.5 times longer were found for several hydrofluoro(poly)ethers when the temperature dependence was considered (Myhre et al., 1999). When calculating OH-based lifetimes, the use of 272K as an average tropospheric temperature, and methyl chloroform (CH_3CCl_3), as a chemical of well known sources and sinks, has been suggested (Spivakovsky et al., 2000) to minimize the errors resulting from neglecting the specific temperature dependences.

Generally, HFEs show low surface sticking coefficients and low water solubility. Thus, primary removal of HFEs in the troposphere will mainly be initiated by reaction with OH radicals. Although global atmospheric abundance of OH radicals is around 2 orders of magnitude greater than that of chlorine atoms, Cl reactions are generally faster than OH reactions, $k_{\text{Cl}}/k_{\text{OH}} \geq 10$, so their contribution to the degradation of organic compounds may be not negligible compared to the role of OH (Finlayson-Pitts & Pitts, 2000). The contribution of Cl to the oxidation of HFEs could be significant in areas where the concentration of Cl precursor species has been reported to be high, such as the coastal boundary layer (Spicer et al., 1998).

The influence of the tropospheric temperature profile on the Cl rate constants has been studied and reviewed for many halocarbons (IUPAC, NASA). Recently, this has been done for HFEs as well. As it has been shown for OH reactions, the understanding of the kinetic rate constants as a function of temperature is required to properly evaluate the contribution of Cl reactions to the degradation of HFEs. The use of the rate constants at only 298K tends to overestimate the global degradation rates of both OH and Cl reactions, given the decrease of T with altitude. The degree of overestimation may be different for OH and Cl depending on the specific value of E_a . The data on temperature dependence are thus crucial to quantify the absolute roles of OH and Cl, and their relative contributions.

In this work we will report the results obtained in the absolute kinetic study of the reactions of Cl atoms with different CFC substitutes (four segregated HFEs), at temperatures ranging from 234-343K, thus providing useful data to simulate the temperature profile characteristic of the troposphere.



To conclude, we will discuss some different strategies that can be used to design CFC substitutes with low environmental impact. For this, computational chemistry offers an alternative to the experimental procedures currently used to assess environmental compatibility parameters such as, lifetimes, reaction mechanism or GWP. In the present work, we will evaluate the radiative ability, and hence the contribution to Global Warming, of the HFE-7500, using a recently reported theoretical method based on computational techniques.

Thus, in the Experimental Section we describe the experimental method used in this work. In the Results Section we describe the experimental conditions and we obtain the values for

the rate constants for all the studied reactions at different temperatures, driving to the Arrhenius' expression for each compound. Furthermore, we present a study of the products of the reactions, obtaining the branching ratio for the abstraction channel for each one. In the Discussion Section, we compare the results obtained in this work with previous studies, we discuss the reactivity of the studied compounds taking into account the number of $-CF_2$ -groups in the structure, and, finally, we compare the ionization potential versus the k values for segregated and no segregated HFEs. In the Atmospheric Implications Section, we discuss the atmospheric implications of the studied reactions from the calculus of the lifetimes and GWP for the CFCs substitutes. Finally, in Section 6 (Strategies to design CFC alternatives with low environmental impact: The scope of the computational chemistry), we show and discuss the results obtained for the radiative efficiency of HFE-7500 using new computational techniques.

2. Experimental section

The experimental method used in this work (figure 1) (Aranda et al., 2006; Díaz-de-Mera et al., 2008, 2009), is the absolute discharge flow-mass spectrometry. It incorporates a dual-stage molecular beam system for the sampling. The mass spectrometer was equipped with an electron-impact ion source and a Chaneltron electron-multiplier. The energy level of the ionizing electrons was $E_e=40$ eV. Typical pressures in the first chamber and in the chamber hosting the mass spectrometer were below 1×10^{-6} and $\approx 1 \times 10^{-8}$ Torr, respectively. Both radical and molecular species were fed from the reactor to the first high vacuum chamber through a stainless steel cone (250 μm orifice diameter). They were then channelled through a second stainless steel cone (1000 μm hole diameter) into the mass spectrometer vacuum chamber, as a molecular beam.

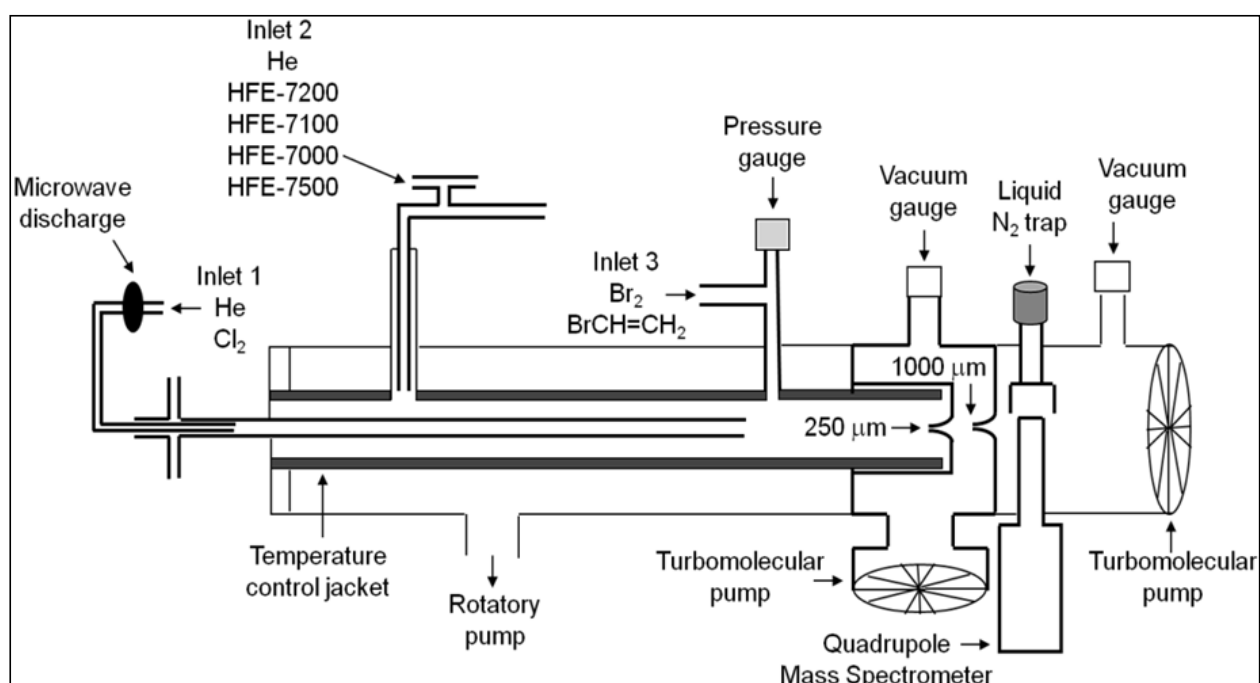
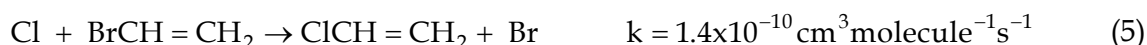


Fig. 1. Schematic view of the experimental set-up.

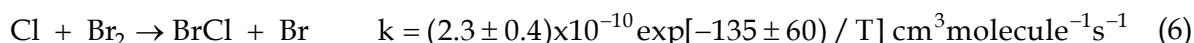
Cl atoms were produced by flowing mixtures of Cl₂ and He through a microwave discharge joined to the main reactor, inlet 1. The discharge tube was coated with phosphoric acid to increase the Cl₂ dissociation yield. To reduce the wall losses of Cl atoms, the inner surfaces of the reactor and the injector were coated with halocarbon wax. HFEs were added through inlet 2 and the reactions with the Cl radicals were observed downstream at the end of the axial injector.

All reactants were diluted in helium and stored in bulbs of known volume. For some experiments, where concentrations of HFEs (7200 y 7100) had to be enhanced, the reactants were used without dilution in helium, directly from the storage bulb. In order to assure constant and accurate HFE concentrations, their flows were regulated with mass flow controllers. The direct detection of the organic compounds was not possible since the mass spectrometer is only able to detect masses just below 200 amu. However, the signals found at $m/e=131$, 69, 120, and 69 for HFE-7200, HFE-7100, HFE-7000, and HFE-7500, respectively, showed good intensity and no overlap with the peaks of the rest of the species.

Molecular chlorine was detected at its parent peak $m/e=70$ and the absolute concentration of Cl atoms was measured by titration with BrCH=CH₂ in excess, and subsequent mass spectrometric detection of ClCH=CH₂ at $m/e=62$ and BrCH=CH₂ at $m/e=106$ (Park et al., 1983):



During a kinetic run (for HFE-7200, HFE-7100, and HFE-7000), the remaining chlorine was observed indirectly as BrCl at $m/e=116$ by scavenging Cl atoms with Br₂ (Aranda et al., 2003). Br₂ was introduced in excess at the end of the reactor through inlet 3, to ensure the complete consumption of Cl atoms by Br₂ (Bedjanian et al., 1998):



For HFE-7500, the remaining chlorine was followed indirectly as ClCH=CH₂ (at $m/e=62$) by scavenging Cl atoms with BrCH=CH₂ (reaction 5). Following both procedures, the detection limit for Cl atoms was 9×10^{11} molecule cm⁻³.

Reagents

Liquid compounds were purified by trap-to-trap distillation. The chemical used were: He (Praxair, 99.999%), Cl₂ (Praxair, >99.8%), Br₂ (Fluka, ≥99.5%), BrCH=CH₂ (Aldrich, 98%), ClCH=CH₂ (Fluka, ≥99.5%), HCl (Aldrich, >99%), HFE-7200 (3M Novec, >99%), HFE-7100 (Fluka, ≥99%), HFE-7000 (3M Novec, >99%), HFE-7500 (3M Novec, >99%).

3. Results

The experimental conditions for four HFEs studied reactions are shown in table 1.

All the kinetic runs were carried out at 1 Torr total pressure in the reactor and under pseudo-first order conditions with the organic compound in excess over Cl atoms. Preliminary experiments were conducted in which the reactions between Cl₂ and Br₂ (or BrCH=CH₂) with HFEs were evaluated. No reaction was observed within the time used in the experiments. Homogeneous losses (Cl-self reaction) did not contribute to the observed temporal profiles because of the low radical concentration (from 0.8×10^{11} to 3.0×10^{11} molecule cm⁻³).

Heterogeneous wall losses of chlorine atoms were checked in additional experiments at all the studied temperatures. These experiments were carried out in the absence of organic compounds, but under similar conditions to those of a kinetic run. In such experiments, with Cl atoms entering the main tube from the injector and Br₂ (or BrCH=CH₂) entering from inlet 3, the formation of BrCl (or ClCH=CH₂) was observed at different contact times. The mean value obtained for the wall loss rate constants was $k_w = 8, 6, 8, \text{ and } 7 \text{ s}^{-1}$ for HFE-7200, HFE-7100, HFE-7000, and HFE-7500, respectively.

Experimental conditions	HFE-7200	HFE-7100	HFE-7000	HFE-7500
T(K)	234-333	234-315	266-333	253-343
P (Torr)			1	
Flow velocity (m s ⁻¹)	600-850	600-800	700-900	650-950
Reaction time (ms)	0-25	0-45	0-43	0-35
[Cl ₂] (10 ¹¹ molecule cm ⁻³)	6-25	2-20	5-6	2.5-7
[Br ₂] (10 ¹³ molecule cm ⁻³)	0.9-50	0.9-50	2.5-8	
[BrCH=CH ₂](10 ¹³ molecule cm ⁻³)				3-7
[HFE](10 ¹⁴ molecule cm ⁻³)	0.04-2.5	0.8-7.0	0.15-2.1	0.03-0.45
[Cl] (10 ¹¹ molecule cm ⁻³)	0.8-1.8	0.8-1.8	2-3	1.1-2
Mixing time for Cl/He (ms)			1.1-0.6	

Table 1. Experimental conditions in the kinetic study of HFES with Cl atoms

For the bimolecular reaction between Cl and HFES, the integrated rate constant that applies to our experimental conditions is

$$\ln [\text{Cl}]_t = \ln [\text{Cl}]_0 - k' t \quad (\text{I})$$

where k' is the pseudo-first-order kinetic rate constant, $k' = k [\text{HFE}] + k_w$. k_w again, represents the heterogeneous wall losses of Cl in the injector. Typical pseudo-first-order decays of Cl (measured as BrCl or ClCH=CH₂), against time are shown in figure 2 for reaction (3) and (4). Similar plots are obtained for HFE-7200 and HFE-7100 reactions.

The pseudo first-order constant values, k' , obtained for the slope, were corrected to take into account the axial and radial diffusion of Cl atoms (Kaufman, 1984) by:

$$k' = k'_{\text{exp}} \left(1 + \frac{k'_{\text{exp}} D}{v^2} + \frac{k'_{\text{exp}} r^2}{48D} \right) \quad (\text{II})$$

where v is the linear flow velocity of the gas mixture in the reactor (cm s⁻¹), r is the radius of the reactor (cm) and D is the effective diffusion coefficient (cm² s⁻¹). The effective diffusion

coefficients of the Cl in He mixture were calculated from the atomic diffusion volumes (Perry et al., 2001). The values obtained within the temperature range used (234-343K) were (330-680), (330-615), (415-680), and (380-650) $\text{cm}^2 \text{s}^{-1}$ for HFE-7200, HFE-7100, HFE-7000, and HFE-7500, respectively. Corrections in k' from diffusion were less than 20, 10, 5, and 8% for HFE-7200, HFE-7100, HFE-7000, and HFE-7500, respectively.

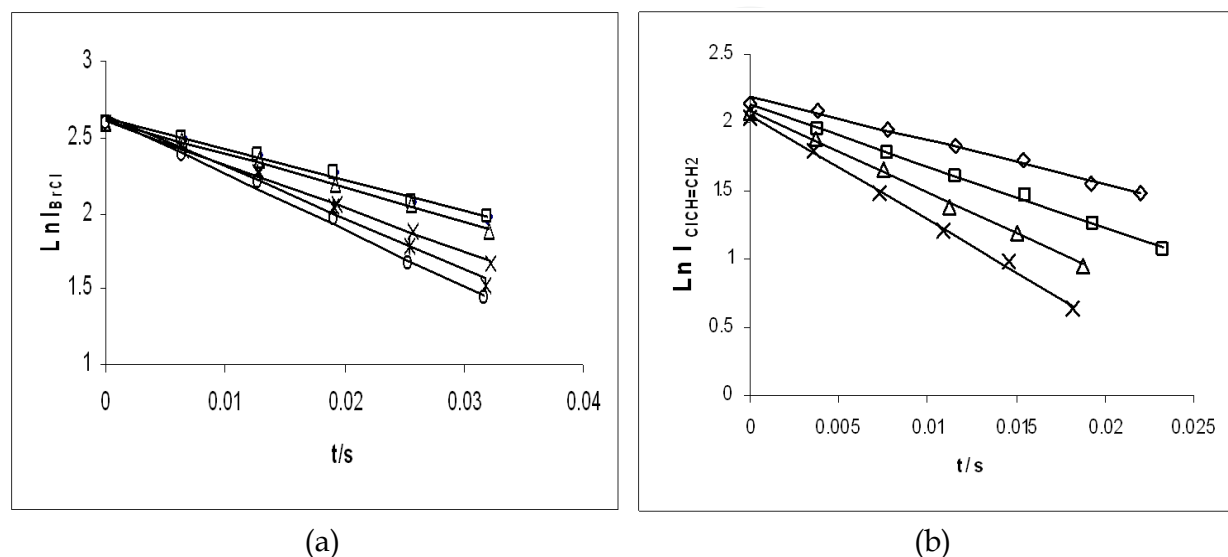


Fig. 2. Typical pseudo first-order decays for Cl for the reaction of a) HFE-7000+Cl at 298K and 1 Torr: [HFE-7000]=0.66 (\square); 0.95 (Δ); 1.35 (\times); 1.85 ($*$); 2.10 (\circ) $\times 10^{14}$ molecule cm^{-3} . b) HFE-7500+Cl at 298 K and 1 Torr: [HFE-7500]=0.53 (\diamond); 0.73 (\square); 1.42 (Δ); 2.09(\times) $\times 10^{13}$ molecule cm^{-3}

HFE-7200		HFE-7100		HFE-7000		HFE-7500	
T(K)	k	T (K)	k	T(K)	k	T (K)	k
234	1.0 ± 0.1	234	1.7 ± 0.7	266	11.7 ± 2.2	253	1.1 ± 0.1
266	1.5 ± 0.1	263	4.6 ± 1.1	273	12.2 ± 2.3	273	1.5 ± 0.1
298	2.1 ± 0.1	273	5.5 ± 0.9	285	13.1 ± 2.2	298	2.2 ± 0.3
315	2.5 ± 0.2	285	7.3 ± 1.5	298	12.4 ± 2.5	307	2.4 ± 0.2
333	3.1 ± 0.4	298	14.3 ± 2.8	315	13.8 ± 2.3	324	2.9 ± 0.3
		315	17.6 ± 2.0	333	16.8 ± 2.6	333	3.3 ± 0.4
						343	3.9 ± 0.5

Table 2. Summary of the second-order rate constants at different temperatures for HFes+Cl reactions. k in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HFE-7200 and HFE-7500, and of $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HFE-7100 and HFE-7000. Errors are 2σ

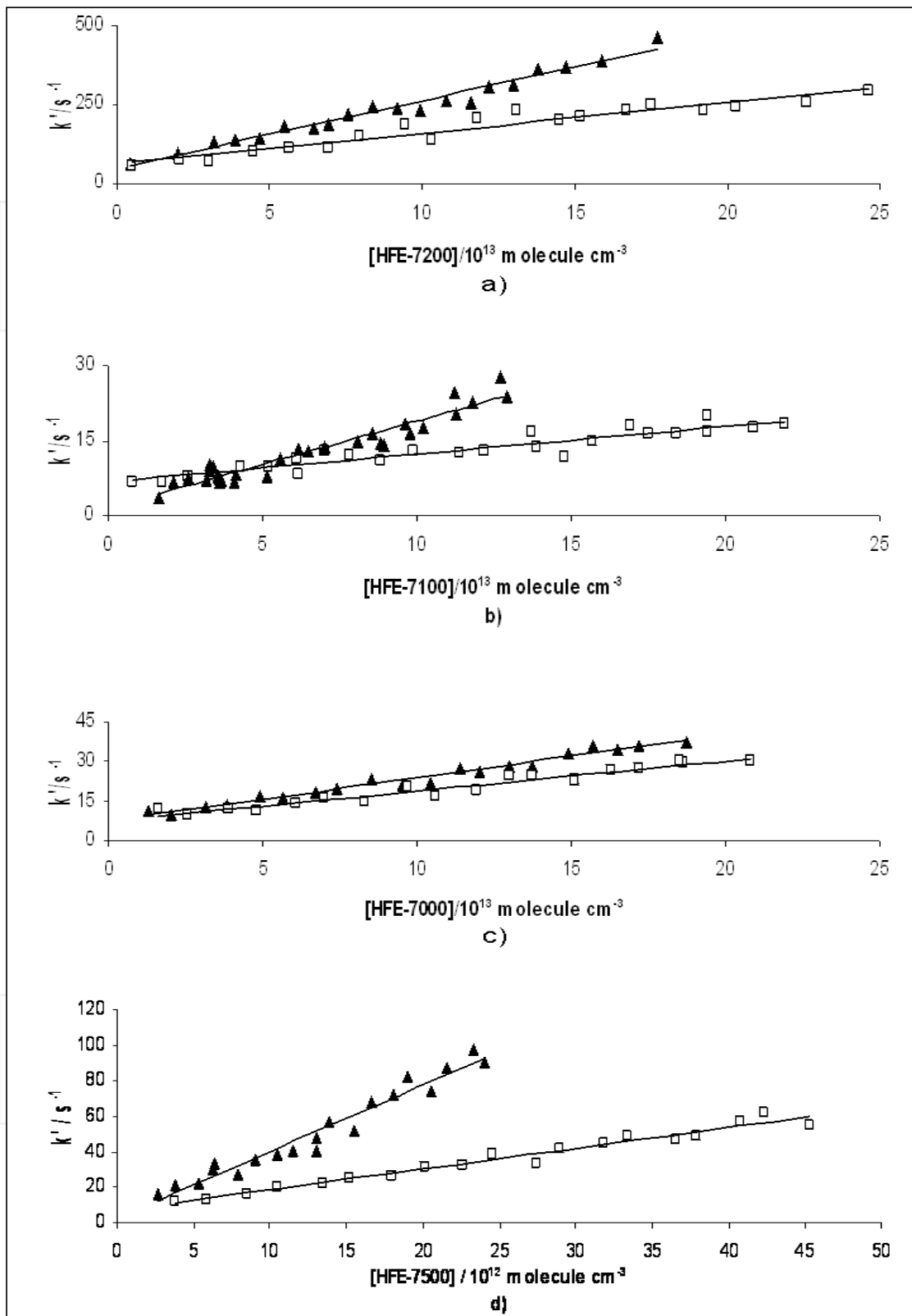


Fig. 3. Plots of the pseudo-first-order rate constants, k' , against segregated HFEs concentrations, at 1 Torr. a) HFE-7200+Cl = (\blacktriangle) 298 K and (\square) 234 K; b) HFE-7100+Cl = (\blacktriangle) 315 K and (\square) 263 K; c) HFE-7000+Cl = (\blacktriangle) 333 K and (\square) 266 K; d) HFE-7500+Cl = (\blacktriangle) 333 K and (\square) 253 K

The second order rate constant was calculated by plotting the pseudo-first-order constant against the HFE concentration and applying weighted least-squares fittings as shown in figure 3. At all temperatures the intercepts agree well with the Cl wall losses measured in the absence of HFEs. Table 2 summarizes the results for all the experimental conditions.

The reaction rate constants were found to increase with increasing temperature for reactions (1) to (4). The Arrhenius equation has been used to fit the rate constant-temperature data:

$$k = A e^{-\frac{E_a}{RT}} \quad (\text{III})$$

Using logarithms:

$$\text{Ln } k = \text{Ln } A - \frac{E_a}{RT} \quad (\text{IV})$$

Plotting Ln k vs. 1/T, the linear weighted, least-squared analyses of the data, yields the activation energy, the pre-exponential factor (errors are 2σ), and allows the calculation of the kinetic rate constant in the studied temperature range at 1 Torr total pressure as shown in figure 4:

$$k(1) = (3.7 \pm 0.5) \times 10^{-11} \exp[-(852 \pm 38) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad T = 234 - 333\text{K}$$

$$k(2) = (2.3 \pm 1.4) \times 10^{-10} \exp[-(2254 \pm 177) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad T = 234 - 315\text{K}$$

$$k(3) = (6.1 \pm 3.8) \times 10^{-13} \exp[-(445 \pm 186) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad T = 266 - 333\text{K}$$

$$k(4) = (1.2 \pm 0.4) \times 10^{-10} \exp[-(1186 \pm 88) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad T = 253 - 343\text{K}$$

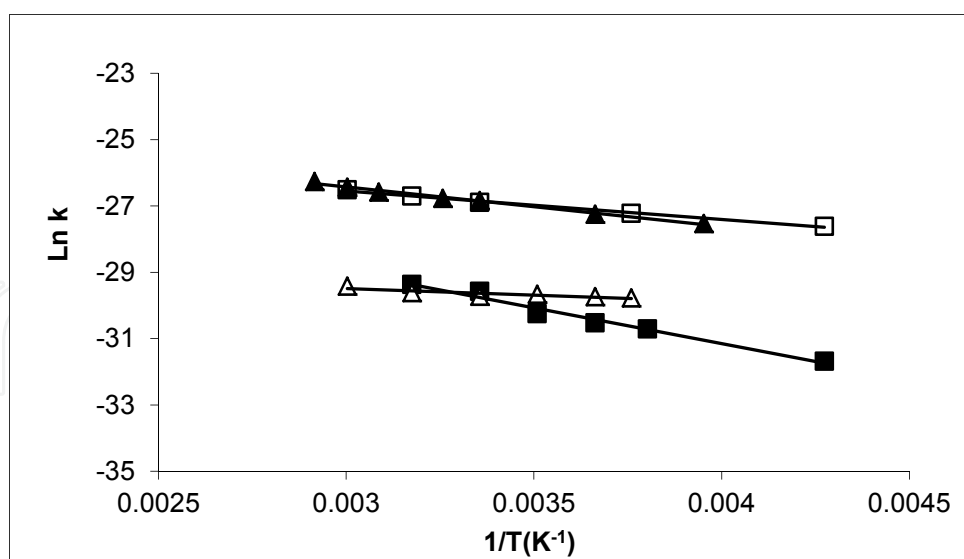
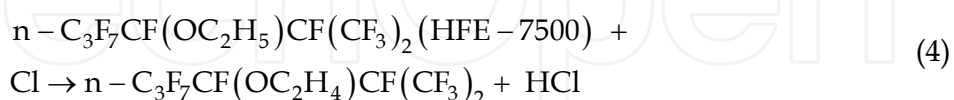
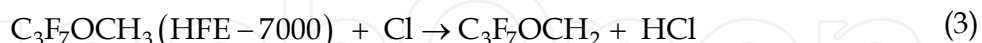
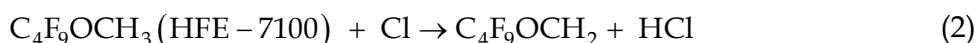


Fig. 4. Temperature dependence of the rate constant for: Cl+HFE-7200 (\square), Cl+HFE-7100 (\blacksquare), Cl+HFE-7000 (\triangle), and Cl+HFE-7500 (\blacktriangle) reactions at 1 Torr total pressure.

Further experiments were also conducted to identify the products of reactions (1) to (4) using higher concentrations of the reactants, in order to enable the detection of possible weak signals. These experiments were carried out at 298K, 1 Torr, and in the absence of Br_2

(or BrCH=CH₂) to avoid secondary chemistry. The expected reaction mechanism is the abstraction of an H atom to form HCl and the corresponding radical:



The masses of the expected radicals, C₄F₉OC₂H₄, C₄F₉OCH₂, C₃F₇OCH₂, and n-C₃F₇CF(OC₂H₄)CF(CF₃)₂ exceed the mass range of the mass spectrometer so they could not be confirmed. The scan for masses up to 200 amu only revealed the formation of HCl whose signals (*m/e*=36 and 38) increased with the time of reaction. No other new peak was observed probably due to the fact that radicals C₄F₉OC₂H₄, C₄F₉OCH₂, C₃F₇OCH₂, and n-C₃F₇CF(OC₂H₄)CF(CF₃)₂ may undergo ionization patterns similar to those of their preceding species. The detection of HCl and the positive activation energy obtained for reactions (1) to (4) are consistent with the expected reaction mechanism, the hydrogen atom abstraction.

Additional experiments were carried out at 298 K and 1 Torr total pressure to measure the yield on HCl of reactions (1) to (4) following the next procedure. To avoid residual contributions present in signals at *m/e*=36 and 38, first, Br₂ (or BrCH=CH₂) in excess was added together with the corresponding HFE (inlet 2), completely removing Cl atoms (giving BrCl or ClCH=CH₂) and avoiding the reaction between Cl and HFE. The residual signals at *m/e*=36 and 38 were obtained under such conditions. Then, Br₂ (or BrCH=CH₂) was changed from inlet 2 to inlet 3, enabling the Cl+HFE reaction and the formation of HCl. Under such conditions Cl is also lost in the reactor's wall. Commercial HCl was used to prepare samples of known concentration to obtain the corresponding calibration plot signal intensity /concentration. The absolute HCl concentrations obtained during the Cl-HFE reactions were, thus, calculated from the HCl signals and the calibration data. The commercial mixtures of HCl were prepared and flowed from time to time testing the signal for a constant flow to the reactor. The intensity of the *m/e* signal remained constant showing the stability of HCl in the storage bulb and glass tubing. No observable heterogeneous wall losses of HCl in the reactor were found. Table 3 shows experimental conditions for these experiments.

Conditions	HFE-7200+Cl	HFE-7100+Cl	HFE-7000+Cl	HFE-7500+Cl
[HFE] (molecule cm ⁻³)	1.3x10 ¹⁴	1.2x10 ¹⁵	6.6x10 ¹⁴	3.5x10 ¹³
[Br ₂] / [BrCH=CH ₂] (molecule cm ⁻³)	(0.7-1.5)x10 ¹⁴	(0.7-1.5)x10 ¹⁴	(0.96-1.4)x10 ¹³	≈ 3x10 ¹³
Reaction Time (ms)	>45	>45	>50	>50
[Cl] ₀ (molecule cm ⁻³)	(1-9)x10 ¹¹	(0.5-7)x10 ¹¹	(1.3-9.1)x10 ¹¹	(2.5-8.5)x10 ¹¹

Table 3. Experimental conditions for the quantification experiments. [Cl]₀ was determined by the titration reaction with BrCH=CH₂ as described in the Experimental Section. Reaction Time is the time used in the experiments, corresponding to >99% of conversion.

For different Cl initial concentrations ($[Cl_0]$) introduced into the reactor and in presence of the HFE, HCl signal produced in reactions (1) to (4) were followed at $m/e=36$ and 38. Figure 5 shows, as an example, the plots for HFE-7200+Cl and HFE-7100+Cl reactions.

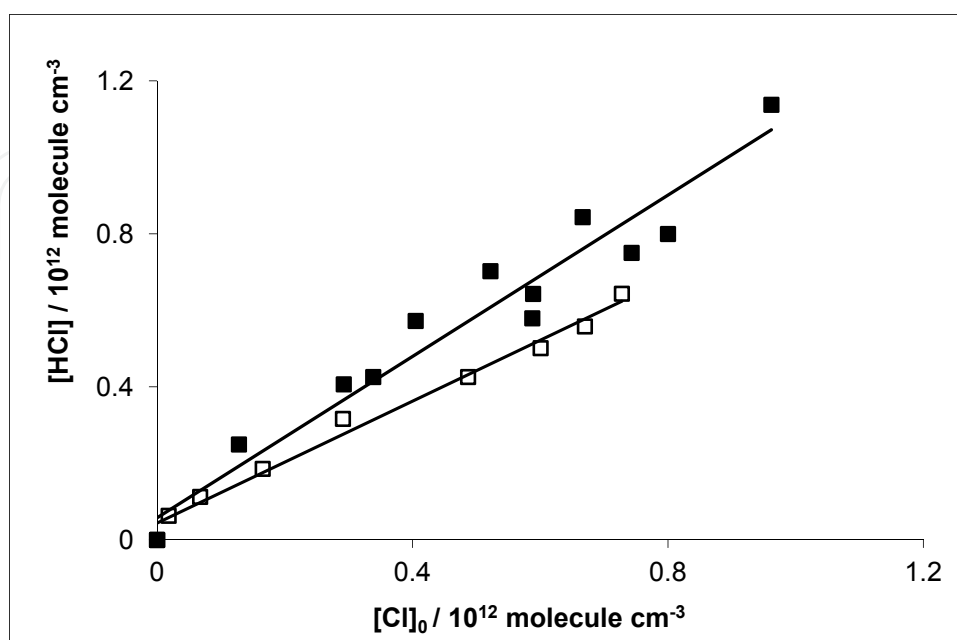


Fig. 5. Yield on HCl. HCl produced against initial Cl atoms concentration at 298 K and 1 Torr total pressure for Cl+HFE-7200 (■) and Cl+HFE-7100 (□) reactions.

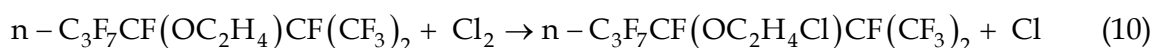
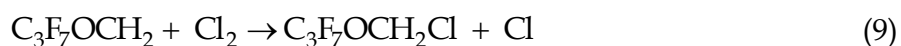
The branching ratio for HCl formation was obtained from the slope and taking into account the competitive losses of Cl in the reactor's wall:

$$\frac{[HCl]}{[Cl]_0} = \frac{k_{\text{abstraction}} [HFE]}{k [HFE] + k_w} \quad (V)$$

Where k is the global kinetic rate constant reported in table 2 (considering the total losses of Cl due to reactions with the HFEs), $k_{\text{abstraction}}$ is the rate constant for the pathway giving HCl, and k_w is the Cl wall losses constant. The obtained results at 298 K and 1 Torr were $k_{\text{abstraction}}/k = 0.95 \pm 0.10$ for reaction (1), 0.88 ± 0.09 for reaction (2), 0.95 ± 0.38 for reaction (3), and 0.98 ± 0.02 for reaction (4) (errors are 2σ). These results confirm that the studied reactions quantitatively proceed through H-abstraction mechanism to form HCl and the corresponding radical. Thus, reactions (1) to (4) are expected to be independent of pressure conditions and the results obtained in this work may apply also to atmospheric pressure conditions.

During the kinetic studies, organic radicals $C_4F_9OC_2H_4$, $C_4F_9OCH_2$, $C_3F_7OCH_2$, and $n-C_3F_7CF(OC_2H_4)CF(CF_3)_2$ could contribute to regenerate Cl atoms through the reaction with Cl_2 present in the reactor (the dissociation efficiency in the microwave discharge was $<100\%$ leaving undissociated Cl_2):





If reactions (7) to (10) were very fast and Cl_2 concentrations in the experiments were high, the net regeneration of Cl would be important and would drive to measured rate kinetic constants lower than real value. To check this possible influence some experimental runs were carried out under the experimental conditions show previously and introducing additional Cl_2 through inlet 2 together with HFEs. The measured rate constants were the same as those obtained in the experiments without additional Cl_2 from inlet 2. Furthermore, as shown previously, the yields for HCl remained constant for large reactions times, also supporting the conclusion that regeneration of Cl through reactions (7) to (10) must be negligible under our experimental conditions.

4. Discussion

In table 4 we report the previous studies for reactions (1) to (4) with the obtained results in this work. Taking into account error limits, the results obtained under low-pressure conditions in this work are in good agreement with those obtained in relative experiments at atmospheric pressure (700 Torr) and room temperature for all the studied HFEs.

Our samples of both HFE-7200 and HFE-7100 were a mixture of two isomers, however in the studies of Christensen et al. (1998) and Wallington et al. (1997), the authors had access to pure samples of n-HFE-7200, n-HFE-7100, i-HFE-7200, and i-HFE-7100 and could study their reactions with chlorine atoms separately. They found no discernible difference in reactivity showing that kinetic rate constant for these isomer mixtures are expected to be independent of composition. These results are important in order to study different commercial mixtures of HFEs.

Comparing the reactivity with Cl for different HFEs of the same series, for example, HFE-7000 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$), and HFE-7100 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$) belonging to $\text{C}_n\text{F}_{2n+1}\text{OCH}_3$ series, we can conclude that there is almost no difference in the reactivity when a $-\text{CF}_2-$ group is introduced in the chain [$(1.24 \pm 0.25) \times 10^{-13}$ and $(1.43 \pm 0.28) \times 10^{-13}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HFE-7000 and HFE-7100, respectively]. Besides the studies showed in table 4, Christensen et al. (1999) studied the reaction with Cl for $n=1$ [$(1.4 \pm 0.2) \times 10^{-13}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] and reactions for $n=2, 3$, and 5 were studied by Nohara et al. (2001) [$(1.1 \pm 0.14, 1.18 \pm 0.14, \text{ and } 1.03 \pm 0.14) \times 10^{-13}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively]. Taking into account the error limits, the results presented in this work are in good agreement with previous studies for this series of ethers, and show that the kinetic rate constant are almost independent of the number of $-\text{CF}_2-$ groups in the perfluorated chain. However, the kinetic rate constants are very sensitive to the length of the hydrocarbon chain [$(1.43 \pm 0.28) \times 10^{-13}$, and $(2.1 \pm 0.1) \times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HFE-7100 ($\text{C}_4\text{F}_9\text{OCH}_3$) and HFE-7200 ($\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$), respectively]. For the same perfluorated chain, the kinetic rate constant increases with the number of $-\text{CH}_2-$ groups in the HFE molecule, what is expected because increases the number of H atoms which can be attacked by Cl.

Furthermore, if we compare the reactivity for HFE-7500 and HFE-7200, considering both of them as ROC_2H_5 [$(2.3 \pm 0.7) \times 10^{-12}$, and $(2.1 \pm 0.1) \times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively], we can see that there is almost no change in the reactivity of this series when the number of $-\text{CF}_2-$ is changed, even if the per-fluorinated chain is ramified (HFE-7500). This conclusion

can be very useful because changing R, we can obtain fluorinated compounds with a particular physico-chemical properties for a specific use without altering their atmospheric reactivity.

Reaction	T (K)	k(298 K) (cm ³ molecule ⁻¹ s ⁻¹)	E _a /R (K)	P (Torr)	References
HFE-7200 + Cl	234-333	(2.1 ± 0.1)×10 ⁻¹²	852±38	1	This work
	296	(2.7 ± 0.6)×10 ⁻¹²		700	[Christensen, 1998] Relative
HFE-7100 + Cl	234-315	(1.43 ± 0.28)×10 ⁻¹³	2254±177	1	This work
	298	(0.97± 0.14)×10 ⁻¹³		700	[Wallington, 1997] Relative
HFE-7000 + Cl	266-333	(1.24± 0.25)× 10 ⁻¹³	445±186	1	This work
	298	(1.18± 0.14)×10 ⁻¹³		700	[Nohara, 2001] Relative
	295	(0.91± 0.13)×10 ⁻¹³		700	[Ninomiya, 2000] Relative
HFE-7500 + Cl	253-343	(2.22 ± 0.28)×10 ⁻¹²	1186 ± 88	1	This work
	298	(2.3 ± 0.7)×10 ⁻¹²		700	[Goto, 2002] Relative

Table 4. Rate constants for the reaction between the Cl radical and the title compounds. Errors are 2σ

Any H atom in the aliphatic chain is susceptible to an oxidant attack. Generally, the radicals (OH, NO₃, Cl, etc.) will tend to abstract the most weakly bound hydrogen atom in the molecule (Seinfeld & Pandis, 1998). Unfortunately, our mass spectrometer was not able to provide the experimental direct evidence of the Cl reaction on the CH₂ or the CH₃ group of HFE-7200, and HFE-7500. In the study of Christensen et al. (1999) they showed that Cl predominantly attack the CH₂ group.

The reactivity on the CH₃ terminal group is, thus, well isolated from changes in the perfluorated chain by the ether link. This is also clear if we compare k_{HFE-7100} (298K) with the result obtained for the reaction of Cl with CH₃CF₃, k_{298K}=2.6×10⁻¹⁷ cm³ molecule⁻¹ s⁻¹ (IUPAC). Thus, the presence of the fluorinated chain gives them the physico-chemical behaviour for industrial or domestic use while the CH₃- or -CH₂CH₃ groups remain

relatively reactive toward the atmospheric radicals (due to the ether linkage), so driving to relatively low lifetimes and mitigating the contribution as greenhouse gases.

The results obtained for E_a/R (852, 2254, 445, and 1186 K for reactions (1) to (4), respectively) are very similar to the obtained for other reactions of Cl with HFEs (Kambanis et al., 1998; Papadimitriou et al., 2004). For example, Papadimitriou et al. (2004) obtained E_a/R values of 929 and 1112 K for reactions of Cl with $\text{CHF}_2\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$, respectively. Also, for many halocarbons with high Cl or F substitution, E_a values are the same order of magnitude to that obtained in this work (IUPAC): $E_a/R = 2000, 2420, \text{ and } 3720$ K has been obtained for reactions of Cl with CH_3CFCl_2 , $\text{CH}_3\text{CF}_2\text{Cl}$, and CH_3CF_3 (IUPAC).

Segregated and no segregated HFEs

The significant decreases in the lifetimes of segregated HFEs compared to non segregated HFEs is attributed to the direct activating effect of the oxygen on the contiguous carbon with CH bonds. In general, the strength of the C-H bonds in hydrofluoroethers depends on the interplay of two counteracting electronic effects: a) the strengthening due to the electron-withdrawing inductive effects of F and/or O atoms through σ -bonds, and b) the weakening of the adjacent C-H bonds due to the π -electron transfer from F or O atom to the central C atom (Papadimitriou et al., 2004).

On the other hand, the inductive effect caused by an F atom is usually more important than their conjugative effect, contrary to the O atom. Taking into account both aspects, we can say that if the O atom is directly bonding to C of C-H bond, this O atom will produce a conjugative effect very important, decreasing the bond strength and so, enabling the abstraction of the H atom. In terms of stability we can say that the conjugative effect of O becomes more stable the C supporting the odd electron after the H abstraction. The inductive effect of F atoms directly bonding to C-H removes electronic density destabilizing the possible radical, and so, causing more difficult the breaking of C-H bond.

The strength of the more labile bond in a molecule can be indirectly measured by means of their ionization potential (IP) as shown in figure 6, in which we can distinguish three different behaviours. In the first group (left in the plot), we found the no fluorinated ethers, like $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$. In these ones, the absence of F atoms and the weakness C-H bonds drives to low IP and high k values.

In the right side of the plot are located the no segregated HFEs because they present high IP and very low k values. This behaviour is in agreement with the described above about the inductive and conjugative effects. Finally, the segregated HFEs are located in the intermediate zone of the plot. This type of HFEs presents all the F atoms in one side of the ether group and the H atoms to the other side. This situation is similar to the hydrogenated ethers, where the conjugative effect of the O is very important in order to make the breaking of the C-H bonds easier. Furthermore, the inductive effect of $-\text{CF}_2-$ and $-\text{CF}_3$ groups over the C-H bonds are attenuated by the fact that these groups are separated of the hydrocarbon chain. This attenuation of the fluorocarbon chain can be appreciated comparing HFE-7000 ($\text{C}_3\text{H}_7\text{OCH}_3$) and HFE-7100 ($\text{C}_4\text{H}_9\text{OCH}_3$). These compounds have similar k values with a different fluorocarbon chain and the same hydrocarbon chain. The HFE-7200 presents an IP value similar to the rest of HFEs segregated and a higher k value because it has a high number of H atoms. The abstraction of H from $-\text{CH}_2-$ group will be easier than from the $-\text{CH}_3$ group due to the conjugative effects of O over the $-\text{CH}_2-$ group.

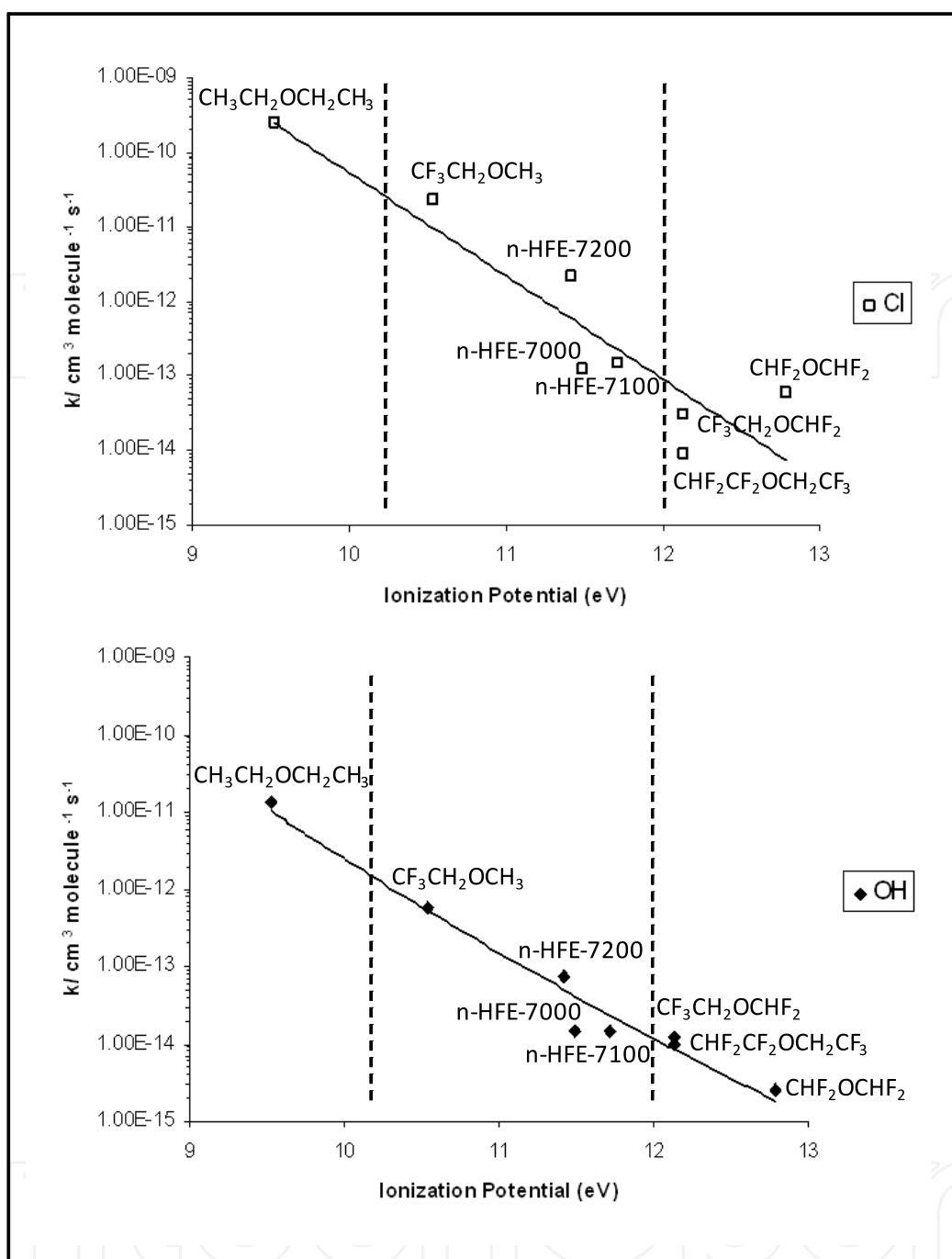


Fig. 6. a) Kinetic rate constants of some HFEs with Cl atoms versus their IP. $k(\text{HFE-7200})$, $k(\text{HFE-7100})$, and $k(\text{HFE-7000})$ from this work; $k(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)$ from Notario et al. (2000); $k(\text{CF}_3\text{CH}_2\text{OCH}_3)$, $k(\text{CHF}_2\text{OCHF}_2)$, and $k(\text{CF}_3\text{CH}_2\text{OCHF}_2)$ from Kambanis et al. (1998); $k(\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_3)$ from Papadimitriou et al. (2004). b) Kinetic rate constants of some HFEs with OH atoms versus their IP. $k(\text{HFE-7200})$, $k(\text{HFE-7100})$, and $k(\text{HFE-7000})$ from this work; $k(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)$ from Mellouki et al. (1995); $k(\text{CF}_3\text{CH}_2\text{OCH}_3)$ from Oyaró & Nielsen (2003); $k(\text{CHF}_2\text{OCHF}_2)$ from Orkin et al. (1999); $k(\text{CF}_3\text{CH}_2\text{OCHF}_2)$ from Zhang et al. (1992); $k(\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_3)$ from Chen et al. (2003). IP of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CF}_3\text{CH}_2\text{OCH}_3$ are experimental data from Bowen & Maccoll (1984) and Molder et al. (1983). The rest of IP is from Papadimitriou et al. (2004).

5. Atmospheric implications

An estimation of the gas-phase lifetime for organic compounds may be obtained for their reactions towards the tropospheric agents. Since oxidative processes against OH radical are the major route of elimination in most of cases, normally the lifetimes are calculated against this OH radical by means of:

$$\tau_{OH} = \frac{1}{k_{OH}[OH]} \quad (VI)$$

However, this equation does not take into consideration the errors due to the vertical temperature profile of the troposphere. Thus, lifetimes estimations for CFCs substitutes are generally calculated on the basis of gas-phase removal by OH only and with methyl chloroform (MCF) as reference:

$$\tau_{OH} = \frac{k_{OH}^{MCF}(272K)}{k_{OH}(272K)} \tau_{OH}^{MCF} \quad (VII)$$

where τ_{OH} and τ_{OH}^{MCF} [$\tau_{OH}^{MCF} = 5.99$ year (Kurylo & Orkin (2003))] are the lifetimes of a given compound and MCF, respectively, due to the reactions with hydroxyl radical in the troposphere only. $k_{OH}(272K)$ and $k_{OH}^{MCF}(272K) = 6.0 \times 10^{-15} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Kurylo & Orkin, 2003) are the rate constants for the reactions of these compounds with OH at 272K. The use of 272K in place of 298K overcomes the problems associated with the use of temperature dependent OH reaction and the errors are minimized compared to estimates using 298K.

Reactions with Cl atoms, and their dependence with temperature, can be especially relevant because, as described in the Introduction, Cl reactions are generally faster than OH reactions and high Cl atoms concentrations have been observed in the marine boundary layer. This fact can significantly affect the mean lifetimes. However, for Cl the transport models are not so developed and its vertical distribution in the troposphere remains rather uncertain, so, an equation similar to (VII) is not available for Cl based lifetimes, τ_{Cl} . Thus, to enable a comparison with OH, τ_{Cl} is estimated from the data obtained in this work at 272K using:

$$\tau_{Cl} = \frac{1}{k_{Cl}[Cl]} \quad (VIII)$$

In table 5 are shown the lifetimes for the studied CFCs substitutes in this work.

In the context of estimating the climate impact of the emissions of these gases, a fundamental parameter is the radiative forcing per unit concentration change, or radiative efficiency (RE); this measures the change in the Earth's radiation balance for a 1 ppbv increase in concentration of the gas. RE values for the studied compounds are included in table 5. The global warming potential (GWP) is one method for calculating the carbon-dioxide equivalent of a 1 kg emission of a gas—it takes into account both the lifetime and the RE of a gas. It is the radiative forcing of an emission of 1 kg at time zero, integrated over some given time horizon, divided by the same value for a 1 kg emission of carbon dioxide. The 100 year GWP is used within the Kyoto Protocol of the United Nations Framework Convention on Climate Change to place emissions on a common scale and IPCC (IPCC) regularly reports 20, 100 and 500 year GWP values for a large number of gases. Table 5 includes the values for these parameters obtained from the global lifetimes (considering OH and Cl degradation) calculated in this work.

As can be seen in table 5, it is clear that the use of rate coefficients determined at 298 K leads to underestimates of the lifetimes by up to a factor of two, which have knock-on effects on the determination of GWPs.

Considering the atmospheric lifetimes, we can see that the HFEs studied would be scavenged mainly by OH radicals. However, it is necessary take into consideration the degradation via Cl radicals because τ_{global} can be considerably modified when we take into account the Cl reactions. Also, under local conditions as in coastal regions or in the marine boundary layer in the early hours where Cl concentrations can be high, the elimination of these compounds via Cl reactions can be even more important than OH reactions.

τ_{global} for HFEs studied are small compared with CFCs. Thus, their degradation processes take place mainly in the troposphere and their transport to the stratosphere is lower than for the CFCs. However, τ_{global} are large enough (>0.5 years) to ensure proper vertical distribution in the troposphere and to minimize the possible isolated smog episodes due to rapid oxidation in the lower troposphere.

Despite having high values for RE, due to the lots of C-F bounds present in these compounds, the obtained values for GWP_{100} are relatively low (<500) compared with CFCs (several miles). Thus, the four HFEs could affect the radiative balance because of the high RE values, but their short lifetimes lead to short-term effect only.

	$\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_3$ HFE-7200	$\text{C}_4\text{F}_9\text{OCH}_3$ HFE-7100	$\text{C}_3\text{F}_7\text{OCH}_3$ HFE-7000	$n\text{-C}_3\text{F}_7\text{CF}(\text{OC}_2\text{H}_5)\text{CF}(\text{CF}_3)_2$ HFE-7500
^a $\tau_{\text{OH}}(298\text{K})$	g0.4	h2.1	i2.1	j1.2
^b $\tau_{\text{OH}}(272\text{K})$	0.9	4.2	4.6	
^c $\tau_{\text{Cl}}(272\text{K})$	3.9	109.5	53.4	4.32
^d $\tau_{\text{global}}(272\text{K})$	0.73	4.08	4.21	1.05
^e RE	^f 0.43	^f 0.38	^f 0.34	^k 0.37
^f GWP_{20}	269	1403	1618	213
^f GWP_{100}	76	401	463	61
^f GWP_{500}	23	122	141	18

^a $\tau_{\text{OH}}(298\text{K})$ has been calculated by means equation (VI) using $k(298\text{K})$, where $[\text{OH}] = 1 \times 10^6$ molecule cm^{-3} (Prinn et al., 2001).

^b $\tau_{\text{OH}}(272\text{K})$ has been calculated by means equation (VII) with $\tau_{\text{OH}}^{\text{MCF}} = 5.99$ year and $k_{\text{OH}}^{\text{MCF}}(272\text{K}) = 6.0 \times 10^{-15}$ cm^3 molecule⁻¹ s⁻¹. k values from Bravo et al. (2010)

^c $\tau_{\text{Cl}}(272\text{K})$ has been calculated by means equation (VIII) using $k(272\text{K})$ obtained in this work, where $[\text{Cl}] = 5 \times 10^3$ molecule cm^{-3} (Pszenny et al., 1993; Wingenter et al., 1996; Spicer et al., 1998).

^d $\tau_{\text{global}}^{-1} = \tau_{\text{OH}}^{-1} + \tau_{\text{Cl}}^{-1}$

^eIn units of W m^{-2} ppbv⁻¹

^fFrom Bravo et al. (2010)

^g $k(298\text{K}) = 7.3 \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹ (Bravo et al., 2010)

^h $k(298\text{K}) = 1.5 \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹ (Bravo et al., 2010)

ⁱ $k(298\text{K}) = 1.5 \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹ (Bravo et al., 2010)

^j $k(298\text{K}) = 2.6 \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹ (Goto et al., 2002)

^kFrom Goto et al. (2002)

Table 5. Several atmospheric parameters for the HFEs studied.

6. Strategies to design CFC alternatives with low environmental impact: The scope of the computational chemistry

The availability of the relationship between molecular structure and the atmospheric oxidation mechanism is the main key in order to determine and design environmentally innocuous materials. The molecular structure can be easily modified to get the desired physical and chemical properties such as thermodynamic behaviour, stability, toxicity, lifetime or radiative properties. For instance, the inclusion of H atoms in the molecular structure is an environmentally advantage since it makes the molecule more reactive against the atmospheric oxidants like OH, Cl, or NO₃. However, an increase of the number of H atoms increases the flammability of the species. On the other hand, an increase on the number of Cl or F atoms increases the lifetimes. Besides, F atoms drive to negligible ozone depletion potential (ODP) parameters compared to Cl atoms. At the meantime, F atoms promote the ability of the molecule to absorb infrared radiation in the atmospheric windows (800-1400 cm⁻¹) what increase the GWPs.

Generally, the studies of the environmental parameters that determine the compatibility of the new CFC alternatives have been undertaken by direct measurement of the compounds' infrared (IR) absorption spectra, kinetic behavior against the tropospheric oxidants (lifetimes) or product distribution and mechanistic studies [see for example: Sihra et al., 2001; Bravo et al., 2010] . From these measurements the radiative forcing of the species is determined, which together with the atmospheric lifetime, then allows an assessment of its GWP. But there are a huge number of molecules which may have industrial or other uses, and it would require a massive investment in time and money to carry out all the measurements required.

Recent studies have shown up that the correct use of computational techniques might be the key to sort out this problem, being a very important tool for the design of CFC alternatives with low environmental impact. In this way, recent researches have indicated that it is possible to calculate infrared spectra using *ab initio* and DFT (Density Functional Theory) methods with useful accuracy, and that radiative transfer models can then be applied to these spectra to determine radiative efficiencies and hence GWPs [Papasavva et al., 1997; Blowers et al., 2007; Bera et al., 2010; etc..].

In the method performed by Bravo et al. (2010b) theoretical spectra for a set of perfluorocarbons were determined using DFT methods. Then, the radiative efficiencies (REs) were determined using the method of Pinnock et al. (1995) and combined with atmospheric lifetimes from the literature to determine global warming potentials (GWPs). Theoretically-determined absorption cross sections were within 10% with experimentally determined values. They found that the calculated RE is extremely sensitive to the exact position of the C-F stretch at around 1250 cm⁻¹ and the raw calculated frequencies cannot be used directly in radiative transfer models. Thus, they used a combination of theoretical and experimental results to obtain a very precise correction to the band position generated directly from the DFT calculations.

As an example, here we used this method to predict the RE of HFE-7500, which experimentally-determined value is summarized in table 5. In figure 7 we can see an schematic view of this procedure, where the cross section spectra of HFE-7500 has been performed using Gaussian 03 software package at B3LYP/6-31G** level of theory.

The computed wavenumbers were corrected following the expression $\bar{\nu}_{\text{scal}} = 0.977 \bar{\nu}_{\text{calc}} + 11.664 \text{ cm}^{-1}$ to obtain scaled wavenumbers, where $\bar{\nu}_{\text{calc}}$ is the calculated vibrational mode

wavenumber and $\bar{\nu}_{\text{scal}}$ is the empirically-corrected value. These modes can be assumed to be Gaussian in shape and here we use a full width of 14 cm^{-1} to simulate the complete infrared spectrum of HFE-7500. Broadly speaking, the wavenumber position and integrated cross sections are then used to calculate the (instantaneous) REs using the simple Pinnock et al. (1995) method. In this method the radiative forcing function describes the radiation able to get the Earth's surface evaluated over the tropopause. Using this approaching we found a REs of 0.55 and $0.43 \text{ W m}^{-2} \text{ ppbv}^{-1}$ for the $0\text{-}2500$ and $900\text{-}1900 \text{ cm}^{-1}$ wavenumber intervals, respectively. The previous literature value measured for the $900\text{-}1900 \text{ cm}^{-1}$ interval was reported by Goto et al. (2002), and it is 16% lower than the predicted here, 0.37 vs 0.43 . However, differences within 14-25% of existing experimental values provide a valuable data for the REs in order to calculate accurate GWPs values (Blowers et al., 2007; Bravo et al., 2010b). Another advantage of using computational techniques to predict REs and hence GWPs, is the possibility of evaluate the cross-section spectrum over the overall infrared spectral interval, $0\text{-}2500 \text{ cm}^{-1}$, since the range of $0\text{-}700 \text{ cm}^{-1}$ is difficult to measure using commercial infrared spectrometers. This wavenumber range is particularly important due to the radiative forcing function has a maximum there as is illustrated in Figure 7. This effect can be observed in our calculation over the HFE-7500 where the RE increase around 28% whether we include the $0\text{-}900 \text{ cm}^{-1}$ interval in the RE calculation, 0.55 vs $0.44 \text{ W m}^{-2} \text{ ppbv}^{-1}$. Apart from the used on the prediction of radiative properties of molecules, computational techniques have successfully been used to establish reaction pathway in chemical mechanisms along with the predictions of atmospheric kinetic rates and hence lifetimes with relatively good accuracy [see for example: Rodríguez et al, 2010; Garzón et al., 2010].

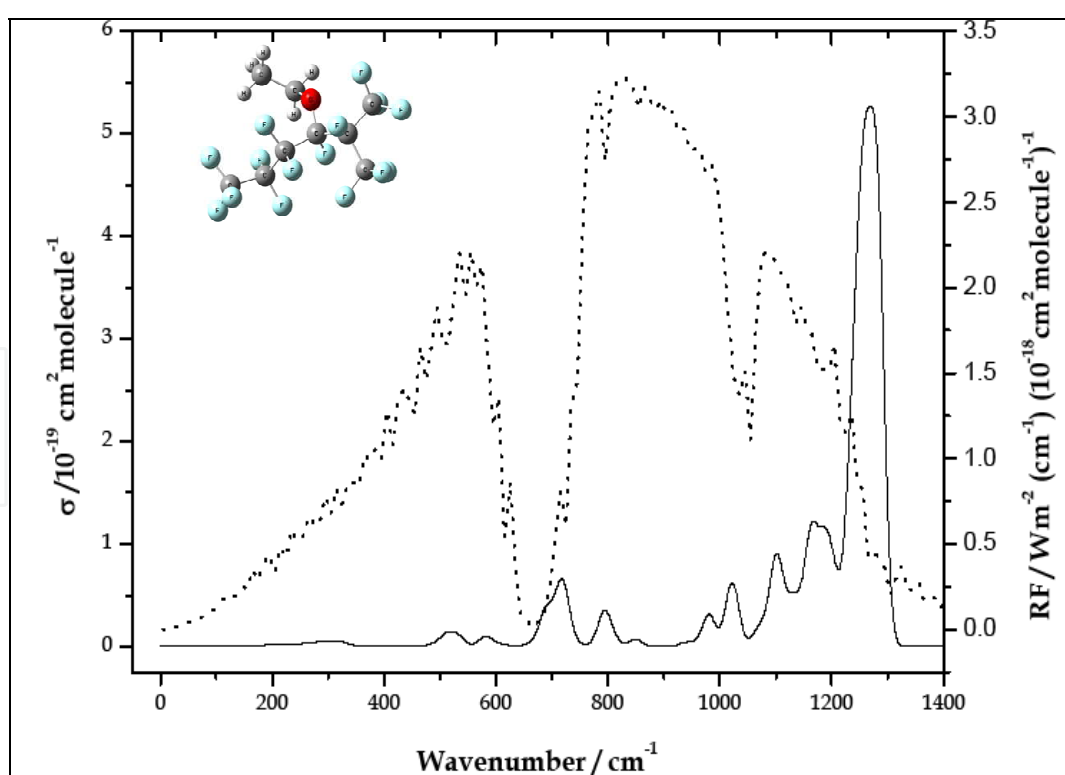


Fig. 7. Simulated infrared cross-section spectrum modeled using Gaussian functions of 14 cm^{-1} full width from the B3LYP/6-31G** vibrational modes for HFE-7500. In dashed lines is represented the radiative forcing function used in the Pinnock et al. (1995) model.

7. Conclusion

Rate coefficients as a function of temperature have been determined for the reactions of Cl with a range of HFEs. The room-temperature data are in good agreement with previous measurements obtained using different techniques and under different conditions. The branching ratio for the abstraction channels of the studied reactions has been determined showing that these reactions proceed almost exclusively via this channel. Using the RE values for these compounds and combining these data with the kinetic data (k values) allows the determination of their GWPs, which are considerably smaller than those for the CFCs that they have been manufactured to replace.

Taking into account the atmospheric aspects and leaving aside the health aspects, we can conclude that segregated HFEs with chemical structures similar to those studied in this work present *a priori* an acceptable environmental compatibility and they can be good substitutes for CFCs: They have a nule contribution to the ozone depletion, a minimum contribution to the smog formation and a low contribution to the greenhouse effect both medium and long term, and a moderate contribution to a short term.

On the other hand, computational techniques are an important and handy key to predict the environmental behavior of new compounds in the atmosphere. Combining different methodology that include the use of physical and chemical software, levels of theory and basic sets, we will be able to calculate environmental parameters such as REs, GWPs or lifetimes. As an example, in this work we have determined a theoretical RE value for HFE-7500, which is in good agreement with previous experimental measurements. This means that when a new compound is proposed to replace a CFC in a determined application because of they have similar physicochemical properties, a right use of these techniques will warns us important information about their environmental behavior. Such information might be very useful for the industry in order to go through with the manufacturing processes. There are several examples where apparently environmentally-safe species have been manufactured and then wrongly used in industrial application. For instance, this is the case of several perfluorocarbons and some hydrofluorocarbons which have been used to replace CFCs in several applications since they do not contain Cl atoms in the structure but they contribute strongly to the global warming. The use of these computational techniques might avoid such wrong uses.

8. Acknowledgment

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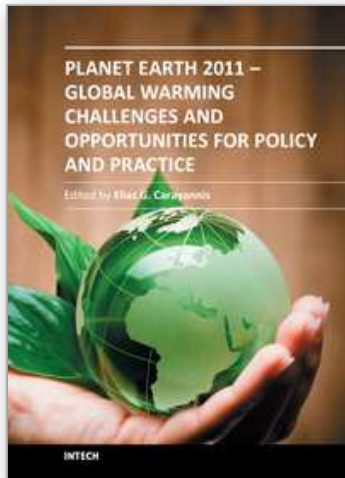
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The failure of the UN climate change summit in Copenhagen in December 2009 to effectively reach a global agreement on emission reduction targets, led many within the developing world to view this as a reversal of the Kyoto Protocol and an attempt by the developed nations to shirk out of their responsibility for climate change. The issue of global warming has been at the top of the political agenda for a number of years and has become even more pressing with the rapid industrialization taking place in China and India. This book looks at the effects of climate change throughout different regions of the world and discusses to what extent cleantech and environmental initiatives such as the destruction of fluorinated greenhouse gases, biofuels, and the role of plant breeding and biotechnology. The book concludes with an insight into the socio-religious impact that global warming has, citing Christianity and Islam.

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