Rate constants for reaction of Cl atoms with hydrofluoroethers[†]

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ABSTRACT: The relative rate technique was used to measure the rate constants for the reactions of Cl atoms with $CHF_2OCH_2CF_3$ and $CHF_2OCHFCF_3$. Experiments were carried out at $296 \pm 2\,K$ and atmospheric pressure using nitrogen as the bath gas. Using 1,1,1-trichloroethane and 1,1,1,2-tetrafluoroethane as the reference compounds, the following rate coefficients were derived: $k(Cl + CHF_2OCH_2CF_3) = (1.14 \pm 0.27) \times 10^{-14}$ and $k(Cl + CHF_2OCHFCF_3) = (1.20 \pm 0.12) \times 10^{-15}$, in units of $cm^3\,molecule^{-1}\,s^{-1}$. The rate constants obtained are compared with the literature data. The implications of the results with regard to the atmosphere are briefly considered. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: rate constants; hydrofluoroethers; chlorine atoms; relative rate method

INTRODUCTION

It is widely known that chlorofluorocarbons (CFCs) cause depletion of stratospheric ozone and contribute to global warming. This has led to an international effort to replace CFCs with environmentally acceptable alternatives. In recent years, partially substituted hydrofluoroethers (HFE) have been suggested as new candidates for CFC alternatives.[1] Since HFE, as well as hydrofluorocarbons (HFCs) do not contain Cl atoms, they do not contribute to stratospheric ozone loss via the well-established chlorine-based catalytic cycles. Therefore, they could be used in applications such as cleaning of electronic equipment, heat transfer agents in refrigeration systems, and carrier fluids for lubricant deposition.[2]

The gas-phase reaction of Cl atoms with organic species represents an important loss process for Cl atoms and organic compounds in the atmosphere.[3] Chlorine atoms are daytime species since they are formed by photolysis of chlorine-containing substances accumulated in the atmosphere during the dark hours. Despite the growing kinetic database for the reaction of Cl atoms with organic compounds there have been relatively few studies on the reaction of Cl atoms with oxygenated organic species.

As part of an ongoing program in our laboratory to study the atmospheric chemistry of oxygenated species, we have used the relative rate technique to investigate the kinetics of the reactions of Cl atoms with $CHF_2OCH_2CF_3$ and $CHF_2OCHFCF_3$ at room temperature and at atmospheric pressure, using N_2 as the bath gas. To the best of our knowledge, this kinetic study is the first experimental determination with a relative rate method using collapsible bags under quasi-real atmospheric conditions of the bimolecular rate coefficient for the reactions of Cl atoms with $CHF_2OCH_2CF_3$ and $CHF_2OCHFCF_3$, which is an anaesthetic widely known as desflurane.

The reaction of Cl atoms with $CHF_2OCH_2CF_3$ has been studied previously by absolute techniques (VLPR[4] and DF-FP[5]) and relative methods (FTIR,[6,7] GC/MS[8]). On the other hand, the reaction with $CHF_2OCHFCF_3$ was measured before using GC/MS as a relative technique. For both reactions we obtained a good agreement with the previous results.

The results obtained will be presented and discussed in terms of the reactivity of these ethers compared to other compounds of similar structure, and used to estimate their lifetimes in the troposphere.

EXPERIMENTAL

Rate constants were measured at $296 \pm 2\,K$ and atmospheric pressure (~ 750 Torr) using a relative rate technique which has been described previously.[9] Reaction mixtures consisting of the HFE and a reference organic

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compound were introduced into an 80 L collapsible Tedlar bag and diluted in N_2.

The initial concentrations used in the experiments were in the range of 110–165 ppm (1 ppm $= 2.46 \times 10^{13}$ molecule cm^{-3} at 298 K and 760 Torr of total pressure) for the HFEs, 110–140 ppm for CH_3CCl_3 and CF_3CH_2F used as reference compounds, and 190–220 ppm for Cl_2. Molecular chlorine was added to generate atomic chlorine by its photolysis, using a set of blacklamps (Philips 30 W) surrounding the Tedlar bag. These lamps provide UV-radiation with a λ maximum around 360 nm. In this study, typically between two and five of these lamps were used to produce atomic chlorine and the time of photolysis varied from 5 to 60 min.

The reaction mixtures were removed from the Tedlar 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 (100–120 Mesh, 2.5 m, 1/8″ i.d.) held at a temperature of 160°C for $CHF_2OCHFCF_3$ and 180°C for $CHF_2OCH_2CF_3$.

The chemicals N_2 (AGA, 99.999%), CF_3CH_2F (Apollo, 99%), $CHF_2OCH_2CF_3$ (Apollo, 97%), and $CHF_2OCHFCF_3$ (Apollo, 99%) were used as received. CH_3CCl_3 (Aldrich, 99.5%) were degassed by repeated freeze-pump-thaw cycling. Molecular chlorine was prepared in our laboratory using the reaction between HCl and $KMnO_4$ and was purified by repeated trap to trap distillation until a sample of 99% purity was obtained, confirmed by IR and UV spectroscopy.

RESULTS

Experiments were performed to measure the relative values of the rate constants of the following reactions at 296 ± 2 K and atmospheric pressure:

$$Cl + CHF_2OCH_2CF_3 \rightarrow Products \quad (1)$$

$$Cl + CHF_2OCHFCF_3 \rightarrow Products \quad (2)$$
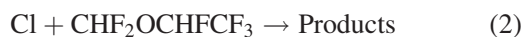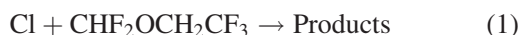
The hydrofluoroether (HFE) and the reference compound react simultaneously with chlorine atoms:

$$Cl + HFE \rightarrow Products \quad (3)$$

$$Cl + Reference \rightarrow Products \quad (4)$$

As described in detail elsewhere,[10,11] the simultaneous decay of the HFE and the reference compound from their initial concentrations at time $t = 0$, [Reactant]$_0$ and [Reference]$_0$, to [Reactant]$_t$ and [Reference]$_t$ at time t is given by Eqn (5):

$$\ln\left\{\frac{[HFE]_0}{[HFE]_t}\right\} = \frac{k_3}{k_4} \ln\left\{\frac{[Reference]_0}{[Reference]_t}\right\} \quad (5)$$

where k_3 and k_4 are the rate constants of reactions (3) and (4), respectively. Thus, a plot of $\{\ln[HFE]_0/[HFE]_t\}$ *vs.*

$\{\ln[Reference]_0/[Reference]_t\}$ should be linear with a slope equal to the ratio of rate constants k_3/k_4.

Prior to carry out the kinetic measurements, to test for potential losses of the HFE or reference compound by dark reactions with Cl_2, mixtures of molecular chlorine 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 chlorine, in the absence of UV light, was of negligible importance over the typical time periods used in this study. Additionally, to test for possible photolysis of the reactants used, mixtures of the reactants in nitrogen, in the absence of molecular chlorine were irradiated using the output of all the black lamps surrounding the chamber for 10 min. Experiments were also carried out with the individual HFE or reference compound alone with Cl_2 under photolysis to ensure that reactions did not produce species with the same retention times as the reactants.

The following was used as a reference reaction to determine the rate constant of reaction (1):

$$Cl + CH_3CCl_3 \rightarrow Products \quad (6)$$

where $k_6 = (9.9 \pm 2.0) \times 10^{-15}$.[12] For reaction (2) the reference reaction was:

$$Cl + CF_3CH_2F \rightarrow Products \quad (7)$$

with $k_7 = (1.50 \pm 0.10) \times 10^{-15}$.[13] All the k values are in units of cm^3 molecule^{-1} s^{-1}.

Figure 1 shows the relative rate data for the reaction (1) with CH_3CCl_3 as the reference compound. The relative rate plot for the reaction of Cl atoms with $CHF_2OCHFCF_3$ using CF_3CH_2F as the reference compound is shown in Fig. 2. Linear least-
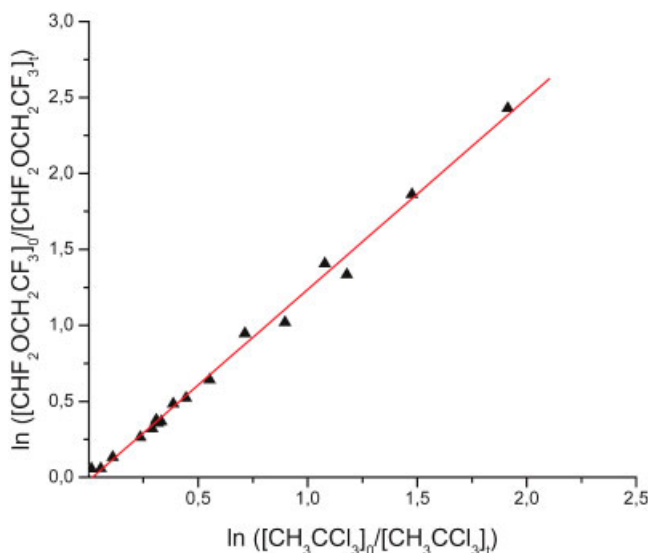

Figure 1. Plot of $\ln([CHF_2OCH_2CF_3]_0/[CHF_2OCH_2CF_3]_t)$ *versus* $\ln([CH_3CCl_3]_0/[CH_3CCl_3]_t)$ for the reaction of Cl atoms with $CHF_2OCH_2CF_3$. The reference compound is 1,1,1-trichloroethane. Seventeen data points from three independent experiments have been plotted
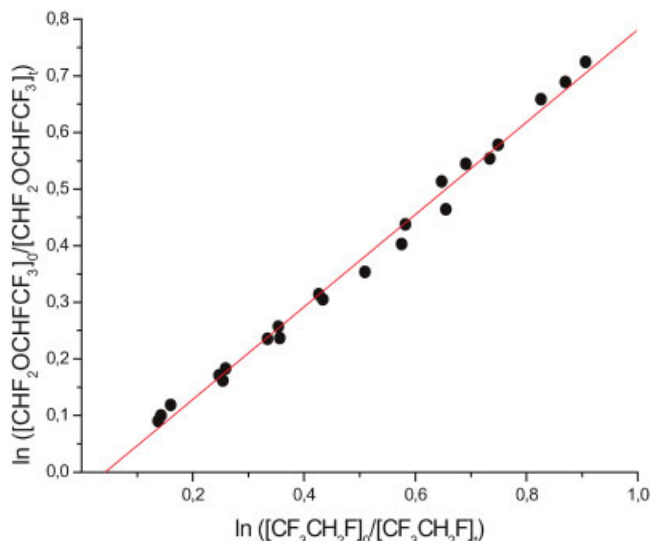
Figure 2. Plot of $\ln([CHF_2OCHFCF_3]_0/[CHF_2OCHFCF_3]_t)$ *versus* $\ln([CF_3CH_2F]_0/[CF_3CH_2F]_t)$ for the reaction of Cl atoms with $CHF_2OCHFCF_3$. The reference compound is 1,1,1,2-tetrafluoroethane. Twenty-two data points from three independent experiments have been plotted

squares analysis of the data in Figs. 1 and 2 gives $k_1/k_6 = (1.15 \pm 0.02)$ and $k_2/k_7 = (0.80 \pm 0.03)$, respectively. The ratios were obtained from the average of several experiments using different initial concentrations of the reactants. Multiplication of these ratios by the literature values for k_6 and k_7 provides two independent determinations of k_1 and k_2. Thus, the derived Cl atoms reaction rate coefficient for $CHF_2OCH_2CF_3$ is $(1.14 \pm 0.27) \times 10^{-14}$ and for $CHF_2OCHFCF_3$ is $(1.20 \pm 0.12) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at (296 ± 2) K and atmospheric pressure.

The linearity of the data points, with correlation coefficients > 0.99, and the fact that the plots show practically no intercepts, suggest that the contribution of secondary reactions with the products of the reactions here studied could be considered negligible. The errors

quoted are twice the standard deviation arising from the least-squares fit of the straight lines and include the corresponding error in the reference rate constant. The uncertainties in the rate constants do not take into account other possible systematic errors, which could be as high as 15–20%.

DISCUSSION

The rate constants for the reactions of Cl atoms with the two HFEs of this study at room temperature are presented in Table 1, where the rate constants for other ethers obtained from the literature have also been included for comparison purposes. Absolute and relative measurements of the rate constant for the reaction of Cl atoms with $CHF_2OCH_2CF_3$ have been previously reported in the literature. The absolute rate constant obtained by Kambanis et al.,[4] using a molecular flow system equipped with a very low pressure reactor, is more than twice the value obtained by Beach et al.[5] using a discharge-flow/resonance fluorescence method. There are also three other previously reported values obtained with relative rate methods, Hickson et al.[6] and Wallington et al.[7] using FTIR spectroscopy and Oyaro et al.[8] employing gas chromatography-mass spectrometry (GC-MS) detection. They are in good agreement within the error limits (Table 1). The value that we obtained, $(1.14 \pm 0.27) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, for this reaction is in good agreement with the average ($\sim 1.25 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}) of the different measurements without considering the result reported by Kambanis et al.[4] It should be noted that the rate constant for reaction (1) is $(0.82 \pm 0.15) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} if we take into account the rate constant of the reference reaction recommended by Sanders et al.,[14] $(7.1 \pm 1.1) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, which is around 28% lower than that given by Platz et al.[12] Therefore, further determinations of the rate

Table 1. Rate constants for the reactions of Cl atoms with haloethers at 296 ± 2 K

Ether	$k_{Cl\ (296\,K)}$ (cm^3 molecule^{-1} s^{-1})	Ref.	Experimental method
$CH_3OCH_2CF_3$	$(2.31 \pm 0.10) \times 10^{-11}$	4	VLPR
	$(1.8 \pm 0.9) \times 10^{-11}$	8	RR-GC/MS
$CHF_2OCH_2CF_3$	$(3.11 \pm 0.14) \times 10^{-14}$	4	VLPR
	$(1.1 \pm 0.1) \times 10^{-14}$	5	DF-RF
	$(1.2 \pm 0.2) \times 10^{-14}$	6	RR-FTIR
	$(1.2 \pm 0.1) \times 10^{-14}$	7	RR-FTIR
	$(1.5 \pm 0.4) \times 10^{-14}$	8	RR-GC/MS
	$(1.14 \pm 0.27) \times 10^{-14}$	This study	RR-GC/FID
$CHF_2OCHFCF_3$	$(1.1 \pm 1.9) \times 10^{-15}$	8	RR-GC/MS
	$(1.20 \pm 0.12) \times 10^{-15}$	This study	RR-GC/FID
$CHF_2OCHClCF_3$	$(3.5 \pm 2.2) \times 10^{-15}$	5	DF-RF
	$(5.4 \pm 0.5) \times 10^{-15}$	7	RR-FTIR
$CF_3OCHFCF_3$	$(6.0 \pm 0.8) \times 10^{-17}$	2	RR-FTIR

VLPR, very low pressure reactor; RR, relative rate; GC, gas chromatography; MS, mass spectrometry; DF, discharge flow; RF, resonance-fluorescence; FTIR, Fourier Transform Infrared Spectroscopy; FID, flame ionization detector.

constant for this reaction are required to solve this discrepancy.

The value of the rate constant for the reaction of $CHF_2OCHFCF_3$ with chlorine atoms that we obtained, $(1.20 \pm 0.12) \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$, is in good agreement with that reported recently in Oyaro *et al.*[8] $(1.1 \pm 1.9) \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$), where the authors explain that the error limit given is essentially determined by the uncertainties in the reaction rate coefficients of the reference compound.

Hydrofluoroethers are expected to react with Cl atoms via an H-atom abstraction mechanism. It is clear from the results in Table 1 that the inclusion of one or more fluorine atoms in an ether changes its reactivity towards Cl atoms. The reactivity of HFEs is expected to depend on several factors, such as the number and position of H atoms, the degree and position of fluorine substitution and the strength of the C—H bond.[4] As demonstrated in earlier studies[4,15,16] the inclusion of an ether linkage in an alkane activates the C—H bonds, an effect which reaches different distances, up to four carbons, from the ether function group.

Substitution of one or more hydrogen atoms in the ether by fluorine atoms leads to a reduction in reactivity of the molecule ($k_{CH_3OCH_2CF_3} > k_{CHF_2OCH_2CF_3} > k_{CHF_2OCHFCF_3} > k_{CF_3OCHFCF_3}$). Thus, the reduction in the reactivity as a result of F substitution in the β C—H bonds on both sides of the —O— linkage seems to be higher than when the substitution is in the α position, in the —CH_2— group. This could be due to the strong electron withdrawing capability of the F atom, obtaining a stronger and less reactive C—H bond.[17] The substitution of the F atom by a Cl atom increased the rate constant ($k_{CF_2HOCFHCF_3} < k_{CF_2HOCClHCF_3}$) probably due to the donation of electron density of the chlorine lone electron pairs to the adjacent carbon centers, resulting in a decrease of the C—H bond strength.

In conclusion, for the fluorinated ethers measured in this study using collapsible bags, the values obtained for the Cl atom reaction rate constants, in comparison with molecules of similar structures, is in agreement with the observed values.

The tropospheric lifetime of the fluorinated ethers studied can be estimated using the following expressions:

$$\tau_{Cl} = 1/k_{Cl}[Cl] \quad and \quad \tau_{OH} = 1/k_{OH}[OH]$$

where k_{Cl} and k_{OH} are the bimolecular rate constants for the reaction of Cl atoms and hydroxyl radicals with a certain fluorinated ether at 296 ± 2 K and in units of $cm^3\,molecule^{-1}\,s^{-1}$, respectively. [Cl] and [OH] are the concentration of atomic chlorine and hydroxyl radicals, respectively. The global average tropospheric Cl and OH concentrations have been estimated as 1×10^4 atoms cm^{-3},[18] and 5×10^5 radicals cm^{-3},[19] respectively. At 296 ± 2 K, the rate constants for the reactions of $CHF_2OCH_2CF_3$ and $CHF_2OCHFCF_3$ with OH have been reported as $(9.1 \pm 1.1) \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$ and

Table 2. Estimated tropospheric lifetimes of HFEs studied with chlorine atoms and OH radicals

Hydrofluoroether	τ_{Cl}[a]	τ_{OH}[a]
$CHF_2OCH_2CF_3$	278	7
$CHF_2OCHFCF_3$	2642	10

[a] Tropospheric lifetime in years.

$(6.5 \pm 0.8) \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$, respectively.[8] The estimated lifetimes of $CHF_2OCH_2CF_3$ and $CHF_2OCHFCF_3$ considering their removal by both Cl and OH are listed in Table 2.

It can be observed in Table 2 that the long tropospheric lifetimes of both ethers clearly indicates that other loss mechanisms, such as transport into the stratosphere, will dominate for these ethers and that the presence of C—F and C—O bonds in their chemical structures allows the HFEs to potentially contribute to the greenhouse effect. Also, it can be seen in Table 2 that the removal of these HFEs from the troposphere will be dominated by their reaction with OH radicals.

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