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PAPER 11

Rate constants and Arrhenius parameters for the reactions of OH radicals and Cl atoms with $\text{CF}_3\text{CH}_2\text{OCHF}_2$, $\text{CF}_3\text{CHClOCHF}_2$ and $\text{CF}_3\text{CH}_2\text{OCClF}_2$ using the discharge flow / resonance fluorescence method

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Professor Richard Tuckett (University of Birmingham) / July 2011

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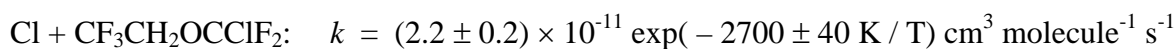
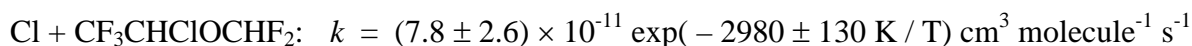
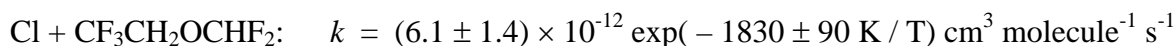
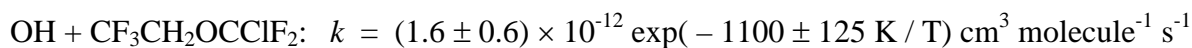
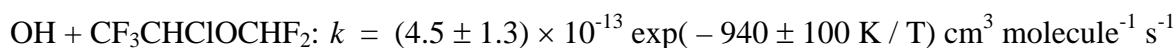
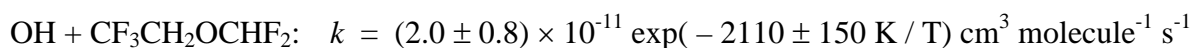
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Rate constants have been determined for the reactions of OH radicals and Cl atoms with the three partially halogenated methyl-ethyl ethers, $\text{CF}_3\text{CH}_2\text{OCHF}_2$, $\text{CF}_3\text{CHClOCHF}_2$ and $\text{CF}_3\text{CH}_2\text{OCClF}_2$, using discharge-flow techniques to generate the OH radicals and the Cl atoms and resonance fluorescence to observe changes in their relative concentrations in the presence of added ether. For each combination of radical and ether, experiments were carried out at three temperatures between 292 and 410 K, yielding the following Arrhenius expressions for the rate constants within this range of temperature:



The results are compared with those obtained previously for the same and related reactions of OH radicals and Cl atoms, and the atmospheric implications of the results are considered briefly.

Introduction

Partially halogenated ethers have uses both as potential replacements for chlorofluorocarbons¹ (CFCs) in a number of applications, and as quite widely used anaesthetics.² Consequently, studies of the kinetics of the reactions of these compounds with free radicals, especially OH, are useful, since the results aid our understanding of their atmospheric chemistry and allow their atmospheric lifetimes to be estimated. Less directly, they assist with the interpretation of laboratory experiments that are designed to reveal the mechanisms by which these ethers break down in the atmosphere.³ Finally, evaluation of the rate constants and activation energies for these reactions can help with the construction of structure-activity relationships. In this context, one can, for example, compare the kinetic parameters for the reactions of a given radical with the substituted ethers with those for the reactions of the same radical with the corresponding substituted alkanes where the ether linkage is absent. Alternatively, one can explore how substitution of fluorine or chlorine atoms for hydrogen atoms affects the susceptibility of the molecule to attack by, for example, OH radicals or Cl atoms.

Hydrofluoroethers (HFEs) are favoured as possible CFC replacements over other halogenated ethers as they contain no chlorine, which if released as atoms can catalytically destroy stratospheric ozone. Of course, HFEs are volatile and will inevitably be released into the atmosphere during use. Their oxidation, initiated predominantly by OH radicals, will lead to the formation of fluorinated esters and fluorinated formates.^{4,5} The likely introduction of HFEs as CFC replacements in some applications has led to a flurry of laboratory activity in the past few years in efforts to understand and quantify their atmospheric chemistry. Both direct^{3,6,7,8,9} and relative rate^{4,5,10,11,12,13} measurements have been undertaken. As the latter often use chlorine atoms to initiate oxidation of the HFEs, direct measurements of both OH radical and Cl atom reactions with HFEs are important.

The halogenated ethers that are employed as anaesthetics do contain chlorine. For this reason, the reactions of some of these compounds with OH have been investigated by Langbein et al.⁹ and Brown et al.¹⁴ to see whether their release could have a significant environmental impact. More recently, Tokuhashi et al.¹⁵ have carried out a very thorough investigation of the kinetics of OH radicals with three hydrochlorofluoroethers (HCFEs): $\text{CHFClCF}_2\text{OCF}_3$, $\text{CHFClCF}_2\text{OCHF}_2$ and $\text{CF}_3\text{CHClOCHF}_2$. The last named of these HCFEs, widely called isoflurane, is an anaesthetic that can be manufactured by photochlorination of $\text{CF}_3\text{CH}_2\text{OCHF}_2$,¹⁶ an HFE which is sometimes called FEFME. It was this process which prompted an earlier study¹² from our laboratory of the kinetics of the reactions of Cl atoms with $\text{CF}_3\text{CH}_2\text{OCHF}_2$, $\text{CF}_3\text{CHClOCHF}_2$ and $\text{CF}_3\text{CH}_2\text{OCClF}_2$, the last being a by-product of the photochlorination of FEFME to isoflurane.

In the present paper, we report direct rate measurements on the reaction of Cl atoms and OH radicals with the same three halogenated ethers $\text{CF}_3\text{CH}_2\text{OCHF}_2$, $\text{CF}_3\text{CHClOCHF}_2$ and $\text{CF}_3\text{CH}_2\text{OCClF}_2$, using the discharge-flow technique. Decays in the concentration of Cl or OH were observed using resonance fluorescence. Rate constants are reported for three temperatures between 292 and 410 K and our results are compared with the limited kinetic data in the literature.

Experimental Method

The experiments were carried out in a Pyrex flow tube (length 1.5 m and internal diameter 2.2 cm) which was fitted with a sliding injector fitted with a showerhead end to ensure rapid mixing of the molecular species introduced into the main flow *via* the injector. The inner wall of the main flow tube was coated with halocarbon wax to minimise any heterogeneous loss of Cl atoms and OH radicals. The central part of the flow tube (length 1.3 m) was surrounded by a double jacket. Heated fluid could be passed through the inner of these two jackets to provide temperatures above room temperature.

A large right-angle stopcock at the downstream end of the flow tube could be used to control the flow of gas through the tube. The observation station was located just before this stopcock. It consisted of an anodised aluminium block (*ca.* $7.5 \times 7.5 \times 7.5$ cm) to which a microwave-powered lamp for exciting resonance fluorescence and a photomultiplier tube (PMT) for observation of the fluorescence were attached.

Cl atoms were observed *via* their resonance fluorescence, mainly in the $(4s^13p^4)^4P_{3/2} \rightarrow (3p^5)^2P_{3/2}$ transition at 137.96 nm. The incident light was supplied by passing a dilute mixture of Cl₂ (*ca.* 0.1%) in argon through a microwave discharge (EMS, Microtron 200). The gas pressure in this lamp was set at *ca.* 0.8 Torr. This lamp was attached to a 5 cm long horizontal side-arm that was coupled to the aluminium block and terminated in a BaF₂ window, which was common to both the lamp and the baffle arm. BaF₂ cuts out radiation below *ca.* 136 nm, thereby discriminating against atomic oxygen emission lines at wavelengths between 130.2 and 130.6 nm, and which might be generated in the lamp from impurities containing oxygen. Before entering the flow tube, light from the lamp passed through a series of simple baffles to reduce any signal from scattered light. On the opposite side of the aluminium block was an anodised aluminium light trap designed to further reduce the level of scattered light. For these experiments a solar blind PMT (Electron Tubes, type 9403) was placed vertically above the flow tube and orthogonal to the lamp. The fluorescence passed through a CaF₂ window on the side of the side of the metal block. A second baffle arm was used to discriminate against fluorescence from scatter and a MgF₂ lens mounted in this baffle arm gathered this light and directed it onto the PMT. The tube between this lens and the front window of the PMT was evacuated during measurements on Cl atoms. The amplified signal from the PMT was recorded on a chart recorder.

OH radicals were detected by resonance fluorescence in the (0,0) band of the $A^2\Sigma^+ - X^2\Pi$ band system at *ca.* 309 nm. The lamp and PMT were attached to the same block as used in the experiments on Cl atoms and the optics and baffles were also unchanged. To excite resonance fluorescence from OH radicals, we employed the same lamp as before but now OH $A^2\Sigma^+ - X^2\Pi$ emission was supplied by passing a flow of helium saturated with water vapour through the same microwave discharge cavity. The pressure in the lamp was kept at *ca.* 15 Torr. In these experiments, fluorescence passed through a narrow band interference filter (Corion, centre wavelength 310 ± 2 nm, bandwidth (FWHM) 11 ± 2 nm) before reaching the PMT (EMI, 9781B). Again the amplified signals from the PMT were recorded on a chart recorder.

Cl atoms were generated upstream of the main flow tube by passing a very dilute mixture of Cl₂ in helium through a microwave discharge (EMS, Microtron 200). To estimate the flow of atomic chlorine and their rate of loss on the flow tube walls, they were titrated with NOCl

($k_{298} = 8.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ¹⁷) introduced through the moveable injector.. This gas flow was combined with the main diluent flow and passed along the flow tube. It was estimated that the minimum detectable concentration of Cl atoms in our system, at a signal-to-noise of 1:1, was *ca.* $3 \times 10^9 \text{ molecule cm}^{-3}$. Most of our kinetic experiments were performed with an initial Cl atom concentration of *ca.* $7 \times 10^{10} \text{ molecule cm}^{-3}$. OH radicals were generated upstream of the main flow tube by passing a very dilute mixture of F₂ in helium through a microwave discharge (EMS, Microtron 200) and reacting the resultant F atoms with a large excess of H₂O ($k_{298} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ^{17,18}).

Halogenated ethers were introduced through the moveable injector. In experiments at elevated temperatures, the tip of the injector was at least 5 cm inside the heated section of the flow tube for all measurements. All experiments were carried out with helium as the main carrier gas. Linear flow velocities between 17 m s^{-1} and 27 m s^{-1} were employed. Gas flows were monitored using calibrated gas flow controllers (Bronkhurst Hi-Tec and MKS Instruments) and the total pressure in the flow tube was measured with a 0–10 Torr Baratron pressure gauge.

In agreement with the findings of others, measurements on both Cl atoms and OH radicals, performed in the absence of added halogenated ether, showed that the resonance fluorescence at the observation point increased as the sliding injector was withdrawn. This effect is due to the reduction in the loss of atoms or radicals on the outside wall of the sliding injector as less of it is exposed to the flow of atoms or radicals. For such measurements plots of $\ln(I_{\text{RF}})_x$ *versus* x , where $(I_{\text{RF}})_x$ is the intensity of the resonance fluorescence signals from Cl atoms or OH radicals at the distance x from the tip of the injector to the observation point, were linear with a positive slope. When a given concentration of a halogenated ether was added, its initial concentration was always sufficiently large (i.e. [halogenated ether] \gg [X]) to ensure first-order kinetics and to eliminate any effects of secondary reactions. Under these pseudo-first-order conditions, the data obtained could again be analysed by plotting $\ln(I_{\text{RF}})_x$ *versus* x , but now the slope of the observed line was negative as reaction with the ether lowered the concentration of Cl atoms or OH radicals as the gas mixtures passed along the flow tube. Representative plots of $\ln(I_{\text{RF}})$ *versus* x are displayed in Figs.1 and 2.

Pseudo-first-order rate constants ($k_{1\text{st}}$) for reaction between Cl or OH and the chosen concentration of the selected halogenated ether were determined by taking the difference in

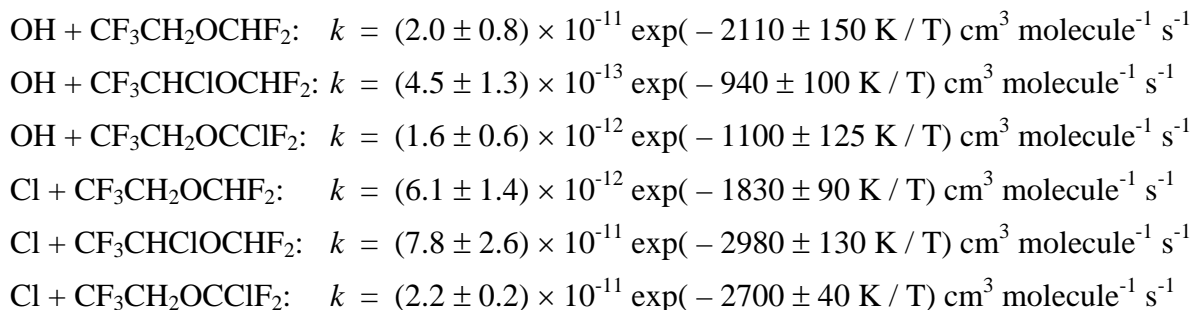
the slopes of the lines in the presence and absence of halogenated ether, like those shown in Figs. 1 and 2, and multiplying the result by the linear flow velocity. The resultant values of k_{1st} , now corrected for the change in heterogeneous loss as the injector was withdrawn, were further corrected to allow for deviations from plug-flow as recommended by Kaufman.¹⁹ The diffusion coefficients for Cl atoms and OH radicals in helium were estimated for the pressure of the experiments (between 2.0 and 3.4 Torr) using the diffusion coefficients for Ar and Ne atoms in helium, respectively. The values of the first-order rate constants that were obtained after applying this correction were always within 3% of those obtained without it.

The halogenated ethers used in the present work were supplied by Rhodia Chemicals with the following levels of purity: $CF_3CH_2OCHF_2$, > 99.8%, main impurity $CHClF_2$; $CF_3CHClOCHF_2$, anaesthetic grade < 50 ppm impurity; and $CF_3CH_2OCClF_2$, > 99.9%, main impurity $CF_3CHClOCHF_2$. These species were subjected to freeze-pump-thaw cycles before use. Analysis by gas chromatography confirmed the stated purities of $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$, but showed a slightly higher level (*ca.* 0.8%) of other ethers present in $CF_3CH_2OCClF_2$. High purity helium (Air Products, GC grade; 99.9995%) and argon (BOC Ltd., 99–99.8%) were used, without further purification, as the carrier gases in the main flow tube and in the resonance lamps, respectively.

Results

As explained in the previous section, each set of experiments like those shown in Figs. 1 and 2 yielded several values of the pseudo-first-order rate constant for different concentrations of the particular halogenated ether which had been added to the gas flow. This type of measurement was repeated several times for each ether with both Cl atoms and OH radicals. Second-order rate constants for the primary reactions, i.e. Cl or OH + halogenated ether, were then determined by plotting the corrected values of k_{1st} against the concentration of added ether, as shown in Figs. 3 and 4. The gradients of the lines from these plots give the values of the second-order rate constants that are listed in Tables 1 and 2. The errors cited in these Tables correspond to 95% confidence limits. The reactions of Cl atoms with $CF_3CHClOCHF_2$ and $CF_3CH_2OCClF_2$ at room temperature are too slow for their rate constants to be measured reliably by the flow tube technique.

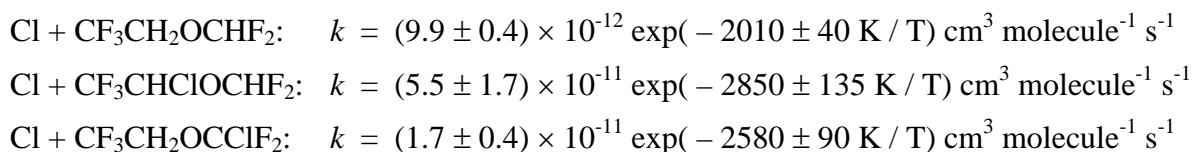
Finally the second-order rate constants, obtained at three temperatures between 292 and 410 K, are presented on Arrhenius plots in Figs. 5 and 6. These plots yield the following Arrhenius expressions:



In these expressions, the errors cited correspond to 2σ .

Discussion

There have been few previous kinetic studies of the reactions of Cl atoms with the three halogenated ethers that have been used in the present experiments. The most extensive experiments are the relative rate measurements made by Hickson and Smith,¹² and those performed by Wallington and co-workers.¹³ Using continuous photolysis of Cl_2 and FTIR spectroscopy to follow changes in concentration, Hickson and Smith¹² measured the rates of the reactions $\text{Cl} + \text{CF}_3\text{CH}_2\text{OCHF}_2$, $\text{Cl} + \text{CF}_3\text{CHClOCHF}_2$ and $\text{Cl} + \text{CF}_3\text{CH}_2\text{OCClF}_2$ relative to the rate for $\text{Cl} + \text{CD}_4$, at temperatures between 295 and 363 K. Their results at room temperature, and those from Wallington's group, are compared with the present data in Table 3. In addition, the rate constants determined at different temperatures by Hickson and Smith¹¹ are displayed on Fig. 5. It can be seen that the data of Hickson and Smith are in fairly good agreement with the present direct measurements, as are the room temperature results of Wallington and co-workers.¹³ Combining the present results with those of Hickson and Smith, giving each set of data equal weighting, yields the Arrhenius expressions:



Coincidentally, the good agreement between these two sets of data serve to confirm the correctness of the rate constants for Cl + CD₄ that were assumed by Hickson and Smith.¹² These values were derived by combining the absolute value of the rate constant for Cl + CH₄ recommended by DeMore *et al.*¹⁷ with the value for the kinetic isotope ratio $k(\text{Cl} + \text{CH}_4) / k(\text{Cl} + \text{CD}_4)$ that was determined by Clyne and Walker.²⁰

Rate constants for Cl + CF₃CH₂OCHF₂ have also been measured by Kambanis *et al.*⁸ They used the VLPR (very low pressure reactor) technique, monitoring reactants and products with a quadrupole mass spectrometer. Although the activation energy which they derived is similar to that which we find, the absolute values of their rate constants are about 2.5 times greater than those found both in the present work and by Hickson and Smith,¹¹ a discrepancy which is well outside the combined error limits.

Given the atmospheric importance of OH radicals, it is not surprising to find that their reactions with halogenated ethers have been studied rather more than those of Cl atoms. Nevertheless, there are not many kinetic data in the literature for the three reactions of OH that have been studied here. DeMore *et al.*,¹⁷ cite an abstract from a meeting presentation by Orkin *et al.*,²¹ which gives $k = 2.6 \times 10^{-12} \exp(-1610 \pm 150 / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for OH + CF₃CH₂OCHF₂. Orkin *et al.* carried out two sets of measurements: discharge-flow experiments with OH concentrations measured by EPR spectroscopy over the temperature range 298 to 460 K, and flash photolysis, resonance fluorescence experiments between 253 and 360 K. Their actual rate constants are in fair agreement with ours, although the Arrhenius parameters differ quite markedly.

For OH + CF₃CHClOCHF₂, Brown *et al.*¹² measured a room temperature rate constant of $(2.1 \pm 0.5) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and Langbein *et al.*⁹ found $(1.7 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Both these results are in good agreement with our value of this rate constant. Tokuhashi *et al.*¹⁵ have carried out extensive measurements on the reaction between OH radicals and CF₃CHClOCHF₂, using both pulsed photolysis and discharge flow techniques at temperatures between 250 and 430 K. Their results are shown in Fig. 6 and again are in good agreement with our own.

It is also of some interest to compare the rate constants for Cl and OH with halogenated ethers with those for the same radicals reacting with the corresponding halohydrocarbons. Unfortunately, this comparison is only possible for the reactions of Cl and OH with CF₃CH₂OCHF₂ and CF₃CH₂CHF₂, since there have been no kinetic data reported previously

for the reactions of Cl and OH with $\text{CF}_3\text{CHClCHF}_2$ and $\text{CF}_3\text{CH}_2\text{CClF}_2$. For Cl atoms the rate constant for reaction with $\text{CF}_3\text{CH}_2\text{OCHF}_2$ at 298 K is about 1.7 times larger than that for $\text{Cl} + \text{CF}_3\text{CH}_2\text{CHF}_2$, whilst the rate constant for $\text{OH} + \text{CF}_3\text{CH}_2\text{OCHF}_2$ at 298 K is twice that for $\text{OH} + \text{CF}_3\text{CH}_2\text{CHF}_2$.

For all three ethers whose reactions have been studied in this work OH radicals react faster than Cl atoms, although the ratio of rate constants at 298 K varies considerably; from 1.1 for $\text{CF}_3\text{CH}_2\text{OCHF}_2$, to 5.4 for $\text{CF}_3\text{CHClCHF}_2$ to 15.2 for $\text{CF}_3\text{CH}_2\text{CClF}_2$. These findings mean that the atmospheric lifetimes of these halogenated ethers will be determined essentially entirely by the rates of their reactions with OH. Taking $[\text{OH}] = 10^6 \text{ molecule cm}^{-3}$ and a mean atmospheric temperature of 288 K, the estimated atmospheric lifetimes are about 2.4 years for $\text{CF}_3\text{CH}_2\text{OCHF}_2$ and $\text{CF}_3\text{CHClOCHF}_2$, and 0.9 years for $\text{CF}_3\text{CH}_2\text{OCClF}_2$.

Acknowledgements

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Table 1 Rate constants for the reaction of Cl atoms with partially halogenated ethers

ether	T / K	rate constant
$\text{CF}_3\text{CH}_2\text{OCHF}_2$	294	$(1.1 \pm 0.1) \times 10^{-14}$
	362	$(3.8 \pm 0.2) \times 10^{-14}$
	398	$(6.3 \pm 0.2) \times 10^{-14}$
$\text{CF}_3\text{CHClOCHF}_2$	318	$(5.9 \pm 0.5) \times 10^{-15}$
	362	$(2.2 \pm 0.2) \times 10^{-14}$
	399	$(4.4 \pm 0.4) \times 10^{-14}$
$\text{CF}_3\text{CH}_2\text{OCClF}_2$	323	$(5.0 \pm 0.3) \times 10^{-15}$
	359	$(1.2 \pm 0.1) \times 10^{-14}$
	402	$(2.7 \pm 0.2) \times 10^{-14}$

Table 2 Rate constants for the reaction of OH radicals with partially halogenated ethers

ether	T / K	rate constant
$\text{CF}_3\text{CH}_2\text{OCHF}_2$	292	$(2.1 \pm 0.3) \times 10^{-14}$
	298	$(1.7 \pm 0.1) \times 10^{-14}$
	347	$(4.2 \pm 0.3) \times 10^{-14}$
	402	$(10.9 \pm 1.2) \times 10^{-14}$
$\text{CF}_3\text{CHClOCHF}_2$	293	$(1.9 \pm 0.2) \times 10^{-14}$
	360	$(3.1 \pm 0.3) \times 10^{-14}$
	393	$(4.3 \pm 0.4) \times 10^{-14}$
$\text{CF}_3\text{CH}_2\text{OCClF}_2$	293	$(3.9 \pm 0.9) \times 10^{-14}$
	298	$(3.6 \pm 0.2) \times 10^{-14}$
	378	$(8.5 \pm 0.9) \times 10^{-14}$
	410	$(10.2 \pm 0.5) \times 10^{-14}$

Table 3. Comparison of rate constants for the reactions of Cl atoms and OH radicals with halogenated ethers

Reaction	T / K	k / cm ³ molecule ⁻¹ s ⁻¹	method ^a	reference
Cl + CF ₃ CH ₂ OCHF ₂	296	$(1.2 \pm 0.2) \times 10^{-14}$	RR (CH ₄ , CD ₄)	Wallington ¹³
	295	$(1.2 \pm 0.2) \times 10^{-14}$	RR (CD ₄)	Hickson and Smith ¹²
	294	$(1.1 \pm 0.1) \times 10^{-14}$	DF/RF	this work
Cl + CF ₃ CHClOCHF ₂	296	$(4.9 \pm 0.5) \times 10^{-15}$	RR (CH ₄ , CD ₄)	Wallington ¹³
	295	$(2.8_5 \pm 0.45) \times 10^{-15}$	RR (CD ₄)	Hickson and Smith ¹²
	298	$(3.5 \pm 2.2) \times 10^{-15}$	DF/RF*	this work
Cl + CF ₃ CH ₂ OCClF ₂	295	$(4.3 \pm 0.7) \times 10^{-15}$	RR (CD ₄)	Hickson and Smith ¹²
	298	$(2.6 \pm 0.4) \times 10^{-15}$	DF/RF*	this work
OH + CF ₃ CH ₂ OCHF ₂	298	$(1.48 \pm 0.06) \times 10^{-14}$	FP/LIF	Tokuhashi et al. ¹⁵
	298	$(1.48 \pm 0.07) \times 10^{-14}$	PLP/LIF	Tokuhashi et al. ¹⁵
	298	$(1.63 \pm 0.08) \times 10^{-14}$	DF/LIF	Tokuhashi et al. ¹⁵
	298	$(1.18 \pm 0.08) \times 10^{-14}$	DF/EPR; FP/RF	Orkin et al ²¹
	298	$(1.7 \pm 0.1) \times 10^{-14}$	DF/RF	this work
OH + CF ₃ CHClOCHF ₂	298	$(2.1 \pm 0.5) \times 10^{-14}$	DF/RF	Brown et al. ¹⁴
	298	$(1.7 \pm 0.4) \times 10^{-14}$	PLP/UVA	Langbein et al.
	293	$(1.9 \pm 0.2) \times 10^{-14}$	DF/RF	this work
OH + CF ₃ CH ₂ OCClF ₂	298	$(3.6 \pm 0.2) \times 10^{-14}$	DF/RF	this work

^a RR(X) - rate measurement relative to that of X; DF/RF - discharge-flow with resonance fluorescence of OH; PLP/UVA - pulsed laser photolysis with detection of OH by longpath ultraviolet absorption; FP/LIF - flash photolysis with laser-induced fluorescence detection of OH; PLP/LIF - pulsed laser photolysis with laser-induced fluorescence detection of OH; DF/LIF - discharge-flow with laser-induced fluorescence detection of OH; DF/EPR - discharge-flow with electron parametric resonance detection of OH.

* evaluation by use of an Arrhenius fit to data obtained at higher temperature

Figure Captions

Fig. 1 Plots of the resonance fluorescence signal from Cl atoms as a function of the distance from the point at which the ether $\text{CF}_3\text{CH}_2\text{OCHF}_2$ was injected into the gas flow to the point at which the resonance fluorescence was observed, for different added concentration of $\text{CF}_3\text{CH}_2\text{OCHF}_2$: $[\text{CF}_3\text{CH}_2\text{OCHF}_2] / 10^{14} \text{ molecule cm}^{-3} = \text{zero (O)}; 7.18 (\sigma); 11.4 (\text{Y}); 16.9 (\text{v}); 27.0 (\text{v}); 32.5 (); 39.6 (\lambda)$. . The temperature in these experiments was 402 K.

Fig. 2 Plots of the resonance fluorescence signal from OH radicals as a function of the distance from the point at which the ether $\text{CF}_3\text{CH}_2\text{OCHF}_2$ was injected into the gas flow to the point at which the resonance fluorescence was observed, for different added concentration of $\text{CF}_3\text{CH}_2\text{OCHF}_2$: $[\text{CF}_3\text{CH}_2\text{OCHF}_2] / 10^{14} \text{ molecule cm}^{-3} = \text{zero (O)}; 3.05 (\text{v}); 6.20 (); 9.40 (\text{v}); 11.5 (\tau); 12.9 (\text{O}); 14.0 (\lambda)$. The temperature in these experiments was 402 K.

Fig. 3 Variation of the pseudo-first-order rate constants for Cl removal, obtained from plots like those shown in Fig. 1, with the concentration of $\text{CF}_3\text{CHClOCHF}_2$ at three different temperatures: 399 K (σ); 362 K (v); 318 K (λ).

Fig. 4 Variation of the pseudo-first-order rate constants for OH removal, obtained from plots like those shown in Fig. 1, with the concentration of $\text{CF}_3\text{CH}_2\text{OCHF}_2$ at three different temperatures: 402 K (σ); 347 K (v); 298 K (λ).

Fig. 5 Arrhenius plots of the rate constants for the reactions of Cl atoms with $\text{CF}_3\text{CH}_2\text{OCHF}_2$ (λ), $\text{CF}_3\text{CHClOCHF}_2$ (σ) and $\text{CF}_3\text{CH}_2\text{OCClF}_2$ (v) derived from the present experiments. For comparison, we show, with the corresponding open symbols, the results of Hickson and Smith¹² obtained using a relative rate technique. The data of Kambanis et al.⁸ for Cl + $\text{CF}_3\text{CH}_2\text{OCHF}_2$ (---◇---), and of Wallington and co-workers¹³ for Cl + $\text{CF}_3\text{CH}_2\text{OCHF}_2$ (∇) and for Cl + $\text{CF}_3\text{CHClOCHF}_2$ (\blacktriangledown) are also shown.

Fig. 6 Arrhenius plots of the rate constants for the reactions of OH radicals with $\text{CF}_3\text{CH}_2\text{OCHF}_2$ (λ), $\text{CF}_3\text{CHClOCHF}_2$ (σ) and $\text{CF}_3\text{CH}_2\text{OCClF}_2$ (ν) derived from the present experiments. For comparison, for OH + $\text{CF}_3\text{CHClOCHF}_2$, we show the room temperature result of Brown et al.¹² and a line (-----) corresponding to the Arrhenius expression determined by Tokuhashi et al.,⁶ both. The recommendation of DeMore et al.¹⁵ for OH + $\text{CF}_3\text{CH}_2\text{OCHF}_2$ is represented by ----O-----.

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