Kinetic Study for the Reactions of Chlorine Atoms with a Series of Hydrofluoroethers

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The absolute rate constants for the reactions of chlorine atoms with several hydrofluoroethers, CHF_2OCHF_2 (**1**), $CF_3CH_2OCH_3$ (**2**), $CF_3CH_2OCHF_2$ (**3**), and $CF_3CH_2OCH_2CF_3$ (**4**), were measured in the gas phase over the temperature range 273−363 K. The experiments were performed with a very low pressure reactor (VLPR) in a molecular flow system, where both reactants and products were simultaneously monitored with a quadrupole mass spectrometer. The absolute rate constants are given by the expressions (in cm^3 $molecule^{-1}$ s^{-1}, 2σ uncertainties): $k_1 = (1.03 \pm 0.19) \times 10^{-12} \exp(-867 \pm 106/T)$, $k_2 = (2.26 \pm 0.20) \times 10^{-11} \exp(0 \pm 50/T)$, $k_3 = (3.84 \pm 1.00) \times 10^{-12} \exp(-1451 \pm 147/T)$, and $k_4 = (4.03 \pm 0.87) \times 10^{-12} \exp(-680 \pm 121/T)$. All reactions proceed via the abstraction of a hydrogen atom and lead to the formation of HCl. The C−H bond strengths of the fluoroethers under study were determined theoretically by ab initio calculations, using the 6-31G basis set, augmented by polarization and diffusion functions. Electron correlation was taken into account by second-order Møller−Plesset perturbation theory (MP2, frozen core). The theoretical results suggest that the C−H bond strengths are increasing in the order $-OCH_2-H < -OCH(CF_3)-H < -OCF_2-H$. Furthermore, the calculated C−H bond strengths are correlated with the corresponding rate parameters for the reactions of Cl atoms with $CF_3CH_2OCH_3$, $CF_3CH_2OCH_2CF_3$, and CHF_2OCHF_2, respectively.

Introduction

Chlorofluorocarbons (CFC's), mainly used as refrigerant and cleaning fluids, are considered as the major threat for the stratospheric ozone protective layer, and therefore their commercial production is banned according to the Montreal Protocol and its subsequent amendments and adjustments.[1] Hydrochlorofluorocarbons (HCFC's) were selected as the first generation of CFC's alternatives, since they are more reactive toward tropospheric species and hence their lifetimes are shorter, preventing their elevation into the stratosphere. Hydrofluoroethers (HFE's) are proposed as a new generation of CFC's alternatives since they do not contain chlorine or bromine atoms and are probably more reactive in the troposphere.[2−8] Although the degradation of hydrofluoroethers in the troposphere most probably occurs through their reaction with OH radicals, a significant part of it may be carried over through a reaction with the less abundant chlorine atoms, due to the higher reactivity of chlorine atoms toward hydrocarbons.[9] It has been proposed that chlorine atoms are generated in substantial concentration over coastal atmospheric environments and their estimated concentration in the marine boundary layer is of the order of 10^4 molecules cm^{-3}.[10] Therefore, it is important to determine the reactivity of HFE's toward chlorine atoms, and evaluate their potential impact to ozone depletion phenomenon. Finally, the reactivity of OH radicals with several HFE's has been studied in the past,[2−6] but the specific reactivity of the different HFE's has not been fully understood.

In this work, the absolute rate constants for the reactions of chlorine atoms with several hydrofluoroethers, CHF_2OCHF_2, $CF_3CH_2OCH_3$, $CF_3CH_2OCHF_2$, and $CF_3CH_2OCH_2CF_3$, were measured over the temperature range 273−363 K. The experiments were performed with the very low pressure reactor (VLPR) method that has been developed and employed successfully by Professor Sidney Benson over the past 20 years.[11] The reactivity of hydrofluoroethers toward Cl atoms is expected to be higher than the corresponding hydrofluorocarbons due to the presence of the ether linkage; however, the specific reactivity of hydrofluoroethers would depend on their molecular structure.

Experimental Section

The title reactions were studied by using a molecular flow system equipped with a very low pressure reactor (VLPR) which has been described previously.[12] In brief, the reaction takes place in a cylindrical Knudsen glass reactor, with two capillary inlets at the upper side and an exit at the lower side connected to a variable aperture system on the first stage of a differentially pumped system. Reactants and products are continuously flowing out of the reactor forming an effusive molecular beam that is modulated by a mechanical fork chopper operating at 200 Hz, before it reaches the ionization region of a quadrupole mass spectrometer (Balzers QMG511). The modulated mass spectrometric signal is amplified by a lock-in amplifier and is further stored on a microcomputer for the subsequent data analysis.

The cylindrical reactor ($V = 168$ cm^3) was thermostated and coated with a thin film of Teflon in order to inhibit wall reactions. The escape constants of various species were determined by monitoring the first-order decay of their mass spectrometric signal after a fast halt of the flow. The escape aperture diameter was 5 mm, and the escape constants of various species were given by the expression $k_{esc,M} = 1.86(T/M)^{1/2}$ s^{-1} where T is the reactor temperature and M is the molecular weight of the escaping species. The flow rates of all gases were determined by monitoring the pressure drop in a known volume, as the gases flowed through a 1 mm × 20 cm capillary. The residence time of all species in the reactor, $1/k_{escM}$, was estimated to be ca. 0.2 s for Cl atoms, while the residence time of HFE's was in the range 0.3−0.4 s.

Chlorine atoms were produced by passing a ∼5% Cl_2/He mixture through a quartz tube that was enclosed in a 2.45 GHz

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TABLE 1: Mass Spectra of CHF_2OCHF_2, $CF_3CH_2OCH_3$, $CF_3CH_2OCHF_2$, and $CF_3CH_2OCH_2CF_3$, at an Electron Energy of 19 EV[a]

CHF_2OCHF_2

m/e	29	31	44	47	48	50	51	99	117
19 eV	7	<1	38	<1	32.5	35.5	100	3	2.5

$CF_3CH_2OCH_3$

m/*e*	15	29	31	33	45	51	61	63	64	69	83	114
19 eV	<1	<1	<1	<1	100	<1	<1	<1	<1	<1	<1	2

$CF_3CH_2OCHF_2$

m/*e*	29	31	33	51	63	64	69	81	83	150
19 eV	9	<1	<1	29	<1	<1	<1	100	9	1.5

$CF_3CH_2OCH_2CF_3$

m/*e*	19	20	29	31	33	50	51	61	63	64	69	83	113
19 eV	42.5	9	<1	13	9.5	<1	<1	31	<1	<1	5	10	100

[a] Intensities are reported relative to the intensity of the most prominent mass peak.

microwave cavity operating at 35 W. The quartz tube was coated with a dried slush of phosphoric and boric acid mixture to inhibit the recombination of Cl atoms. The microwave irradiation conditions ensured a complete dissociation of Cl_2, as verified by the absence of their parent peak at *m*/*e* 70. The mass spectral peak of Cl atoms at *m*/*e* 35 was used to determine their steady-state concentration. The electron ionization energy was set at 19 eV in order to suppress the fragmentation of HCl to Cl^+ (*m*/*e* 35) at negligible levels (~0.3%).

All HFE's were commercially available with a purity 97% for CHF_2OCHF_2, $CF_3CH_2OCH_3$, and $CF_3CH_2OCHF_2$ (Fluorochem), and 99% for $CF_3CH_2OCH_2CF_3$ (Aldrich). They were degassed several times at −78° C in order to remove their impurities. The main impurity of the CHF_2OCHF_2 sample was fluoroethyne $HC{\equiv}CF$, with a parent peak at *m*/*e* 44, which was removed by performing several degassing cycles. The mass spectra of all HFE's at an electron energy of 19 eV, are shown in Table 1. The steady-state concentration of HFE's was determined by monitoring a prominent peak of their fragmentation pattern that is expected to have no significant contribution from the reaction products. For the ethers $CF_3CH_2OCH_3$, $CF_3CH_2OCHF_2$, and $CF_3CH_2OCH_2CF_3$, their mass spectral peaks at *m*/*e* 45 ($CH_3OCH_2^+$), 81 ($CHF_2OCH_2^+$), and 113 ($CF_3CH_2OCH_2^+$) were respectively selected, which could not result from the fragmentation of their corresponding singly dehydrogenated free radicals. For the ether CHF_2OCHF_2, its mass spectral peak at *m*/*e* 51 (CHF_2^+) was selected for monitoring for most experiments; several test experiments were performed by employing its much smaller peak at *m*/*e* 99 (CHF_2OCHF^+) which could not have any substantial interference from the mass spectral fragmentation of the CHF_2OCF_2 radical product. The rate constants derived by using both peaks are differing by ca. 10%, which indicates that the radical CHF_2OCF_2 does not contribute to mass spectrometric peak at *m*/*e* 51. Furthermore, for the slow reactions of Cl atoms with the ethers CHF_2OCHF_2, $CF_3CH_2OCHF_2$, and $CF_3CH_2OCH_2CF_3$, the condition $[HFE] \cong [HFE]_0$ was always satisfied, and hence the rate constants were also derived by assuming pseudo-first-order conditions. The deviations with the rate constants calculated without the pseudo-first-order assumption were less than 5%, which provided a strong evidence for the absence of any mass spectrometric interference from the reaction products in the monitoring of HFE's steady-state concentrations.

TABLE 2: Typical Experimental Data for the Steady-state Concentrations of Cl Atoms and $CF_3CH_2OCH_3$ Molecules as Well as for the Factor $(R - 1)k_{esc,Cl}$ (in s^{-1}), Where $R = ([Cl]_0/[Cl])$[a]

$[Cl]_0$	[Cl]	$[CF_3CH_2OCH_3]_0$	$[CF_3CH_2OCH_3]$	$(R - 1)k_{esc,Cl}$
$T = 273$ K				
4.17	1.77	6.21	2.09	7.07
5.40	1.64	10.90	4.34	11.95
3.92	0.96	11.94	7.03	16.08
3.91	0.90	13.07	8.14	17.35
5.12	0.87	18.83	11.13	25.39
$T = 303$ K				
4.43	1.63	8.78	3.56	9.41
5.60	1.62	11.92	4.71	13.47
7.11	2.01	13.62	4.91	13.93
5.50	1.30	15.50	7.68	17.64
5.50	1.04	17.74	10.47	23.39
$T = 333$ K				
5.04	1.73	10.43	4.58	11.59
3.95	1.20	10.61	5.46	13.18
3.90	1.00	12.36	7.03	16.58
3.85	0.83	14.41	8.92	20.96
3.82	0.82	14.46	9.04	21.11
$T = 363$ K				
2.41	1.21	6.39	3.24	6.41
2.37	0.81	9.41	5.91	12.55
2.73	0.65	14.55	10.52	20.57
2.81	0.55	18.01	13.75	26.41
2.80	0.53	17.55	13.19	27.50

[a] Subscript 0 denotes the steady-state concentration in the absence of the other reactant. All concentrations are expressed in units of 10^{11} molecule cm^{-3}.

The mass spectrometric signal intensity I_M is given by the expression: $I_M = \alpha_M F_M = \alpha_M k_{esc,M} V[M]$, where α_M is a mass spectrometric calibration factor, F_M the flow rate (in molecule s^{-1}), V the reactor volume, and $k_{esc,M}$ the escape constant. The α_M factors for HFE's were determined from accurate calibration curves, by plotting I_M vs F_M. The concentration of Cl atoms was in the range $(0.1-5) \times 10^{12}$ molecules cm^{-3}, while the concentration of HFE's was in the range $(0.001-3) \times 10^{14}$ molecules cm^{-3}. The uncertainty in the mass spectral intensity measurements was ca. 5%; thus the determination of $[Cl]_0/[Cl] = I_{Cl,0}/I_{Cl}$ was determined with an accuracy of ca. 7%.

Results

Mass spectrometric analysis of the reaction products of all title reactions revealed the appearance of HCl (at *m*/*e* 36) as the only reaction product. Typical experimental data for the relatively fast reaction 2 of $CF_3CH_2OCH_3$ with Cl atoms are shown in Table 2, and they show a good mass balance for the consumption of Cl atoms and $CF_3CH_2OCH_3$ molecules ($\Delta[Cl]k_{esc,Cl} = \Delta[CF_3CH_2OCH_3]k_{esc,CF_3CH_2OCH_3}$). However, for the other three much slower reactions (1), (3), and (4), the difference $\Delta[HFE]k_{esc,HFE}$ was very small compared to the corresponding steady-state concentration [HFE], and thus, it was hard to be accurately determined from the mass spectroscopic intensity differences. Several test runs had also confirmed the mass balance for Cl reactant and HCl product, and it was found to be excellent within experimental error for all reactions; titration experiments have shown that the mass spectrometric sensitivity ratio α_{HCl}/α_{Cl} was 1.1 ± 0.1 at 19 eV electron energy.[13] Indeed, for the reactions studied, side reactions producing HCl are impossible, by considering the structure of the HFE's and their corresponding singly dehydrogenated radicals. In addition, there were no secondary radical recombination products detected, a fact consistent with the low-pressure conditions in the reactor.

TABLE 3: Rate Constants of the Title Reactions (in 10^{-14} cm^3 molecule^{-1} s^{-1}, 2σ Uncertainty) at 273, 303, 333, and 363 K

	temperature (K)			
HFE	273	303	333	363
CHF_2OCHF_2	4.35 ± 0.24	5.73 ± 0.30	7.72 ± 0.26	9.38 ± 0.50
$CF_3CH_2OCH_3$	2280 ± 130	2310 ± 101	2270 ± 80	2160 ± 77
$CF_3CH_2OCHF_2$	1.94 ± 0.11	3.11 ± 0.14	4.87 ± 0.17	7.24 ± 0.39
$CF_3CH_2OCH_2CF_3$	33.2 ± 2.3	44.0 ± 3.5	51.2 ± 2.5	62.9 ± 4.2

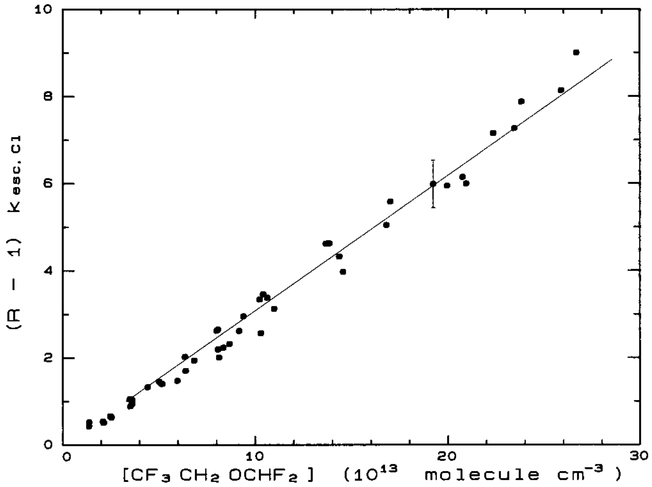
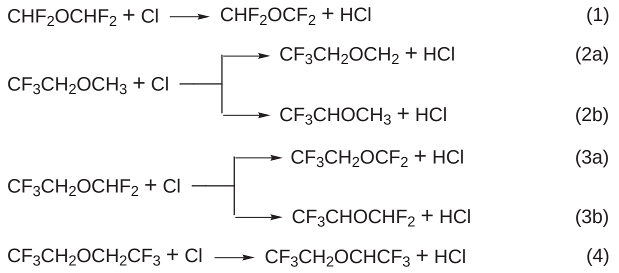


Figure 1. Plot of $(R - 1)k_{esc,Cl}$ vs $[CF_3CH_2OCHF_2]$ at $T = 303$ K. Error bar reflects the propagated error (2σ), solid line is the linear least-squares fit to the data.

Thus, all reactions were occurring via a hydrogen transfer mechanism, and the corresponding kinetic schemes are as follows:



$$CHF_2OCHF_2 + Cl \longrightarrow CHF_2OCF_2 + HCl \quad (1)$$

$$CF_3CH_2OCH_3 + Cl \longrightarrow CF_3CH_2OCH_2 + HCl \quad (2a)$$

$$CF_3CH_2OCH_3 + Cl \longrightarrow CF_3CHOCH_3 + HCl \quad (2b)$$

$$CF_3CH_2OCHF_2 + Cl \longrightarrow CF_3CH_2OCF_2 + HCl \quad (3a)$$

$$CF_3CH_2OCHF_2 + Cl \longrightarrow CF_3CHOCHF_2 + HCl \quad (3b)$$

$$CF_3CH_2OCH_2CF_3 + Cl \longrightarrow CF_3CH_2OCHCF_3 + HCl \quad (4)$$

Application of the steady-state approximation for each reaction leads to the expression:

$$\Delta[Cl]k_{esc,Cl} = k[Cl][HFE]$$

where Δ[Cl] is the steady-state concentrations difference $[Cl]_0 - [Cl]_r$ (subscripts 0 and r denote the absence or presence of HFE reactant, respectively), $k_{esc,Cl}$ is the escape rate of Cl atoms, k is the total rate constant, and [HFE] is the steady-state concentration of the HFE reactant. Upon minor rearrangement, the above expression becomes

$$(R - 1)k_{esc,Cl} = k[HFE]$$

where $R = [Cl]_0/[Cl]_r = I_{35,0}/I_{35,r}$. Therefore, the experimental runs were performed by monitoring the intensity of both Cl atoms and HFE reactant mass spectrometric signals, as the HFE was alternately flowing into the reactor or withheld, at a specific reactor temperature. A typical plot of the above expression for reaction 3 at $T = 303$ K is presented in Figure 1. The linear least-squares fits to the data yield the rate constant k with a precision ca. 10% (2σ). The rate constants of reactions 1, 3, and 4 were also derived by assuming pseudo-first-order conditions, since the steady-state concentration of the corresponding HFE was always much higher that that of Cl atoms, and the agreement between the rate constants calculated by both methods was always better than 5%.

TABLE 4: Rate Parameters for the Reactions of Cl Atoms with HFE's (in cm^3 molecule^{-1} s^{-1}, 2σ Uncertainty)

HFE	$10^{-14}k_{298}$	$10^{-12}A$	E_a/R
CHF_2OCHF_2	5.73 ± 0.30	1.03 ± 0.19	867 ± 106
$CF_3CH_2OCH_3$	2310 ± 101	2260 ± 198	0 ± 50
$CF_3CH_2OCHF_2$	3.11 ± 0.14	3.84 ± 1.00	1451 ± 147
$CF_3CH_2OCH_2CF_3$	44.0 ± 3.5	4.03 ± 0.87	680 ± 121

The experiments were performed at four different temperatures of 273, 303, 333, and 363 K, and the rate constants obtained at each temperature for all HFE's are listed in Table 3. Linear least-squares analyses of the temperature dependence data yield the activation energies and the A factors for all reactions, which are given in Table 4. Finally, the Arrhenius plots of the title reactions are presented in Figure 2.

Discussion

To our knowledge, there is only one recent kinetic study for the reaction of Cl atoms with hydrofluoroethers, that with C_4F_9-OCH_3 at room temperature.[5] However, there are several reaction rates between OH radicals and some HFE's which may be compared with our reaction rates.[2-6] Therefore, all known reaction rate constants of OH radicals and Cl atoms with HFE's at room temperature are presented in Table 5. Furthermore, it is possible to compare to reactivity of HFE's toward Cl atoms and OH radicals with the analogous reactivities of the corresponding hydrofluorocarbons, and these reaction rates at room temperature are presented in Table 6.

The structure−reactivity relationship for these reactions is difficult to be extrapolated from these reaction rates and Arrhenius parameters alone. However, the reactivity of HFE's is expected to depend on several factors, such as the number and position of H atoms, the strength of the C−H bonds, the degree and position of fluorine substitution, as well as the overall molecular geometry. In addition, the ether linkage is expected to play a key role in the reactivity of these compounds.

Comparing the reaction rates of OH and Cl with HFE's in Table 5, it appears that there is no obvious correlation, apart from the fact that the rates of Cl atoms are always higher than those of OH radicals, which is in agreement with the general behavior of hydrocarbons.[9] On the contrary, the reactivity of the corresponding hydrofluorocarbons toward Cl atoms may be lower than toward OH radicals,[16] as can be seen in Table 6. In general, the ether linkage (−O−) activates the neighboring C−H bonds, since the reaction rates of HFE's are always higher than those of the corresponding HFC's, e.g. CHF_2OCHF_2 is 23 times more reactive toward Cl than CHF_2CHF_2. Furthermore, Table 5 indicates that the higher the number of H atoms in HFE's, the greater the reaction rates with Cl atoms result. The examination of the experimental data shows that the presence of CH_xF_y moieties deactivates the neighboring C−H bonds (even through the ether linkage), an effect that becomes weaker as the C−H bond is placed away from the fluorine containing

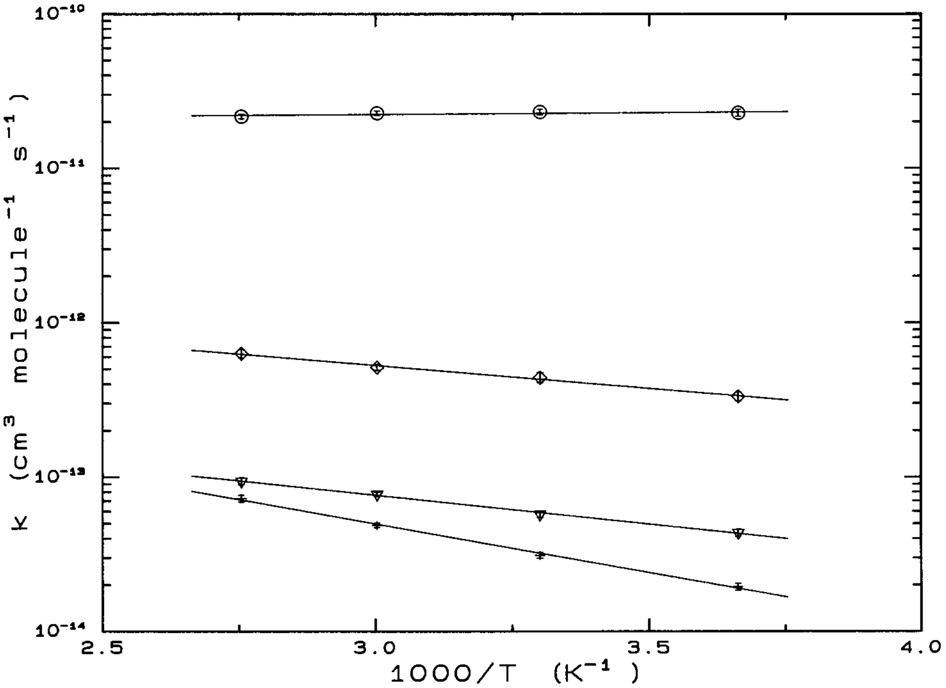


Figure 2. Arrhenius plots for the title reactions. Error bars reflect the propagated errors (2σ), solid lines are the linear least-squares fits to the data. Triangles, reaction 1; circles, reaction 2; crosses, reaction 3; rhombs, reaction 4.

TABLE 5: Room Temperature Rate Constants for the Reactions of Cl Atoms and OH Radicals with HFE's (in 10^{-15} cm^3 molecule^{-1} s^{-1}).

HFE	k_{Cl}		k_{OH}	
CHF_2OCHF_2	57.3 ± 3.0[a]	25.3 ± 2.4[c]	3.0[d]	2.3[f]
$CF_3CH_2OCH_3$	23100 ± 1010[a]	624 ± 67[c]	642 ± 51[e]	
$CF_3CH_2OCHF_2$	31.1 ± 1.4[a]	12.5 ± 0.9[c]	10.7 ± 0.3[e]	
$CF_3CH_2OCH_2CF_3$	440 ± 35[a]		101 ± 15[e]	
$C_4F_9OCH_3$	97 ± 14[b]	12[b]		

[a] This work. [b] Reference 5. [c] Reference 2. [d] Reference 3. [e] Reference 6. [f] Reference 4.

TABLE 6: Ether Linkage Effect on the Rate Constants for the Reactions of OH Radicals and Cl Atoms with HFC's, and Corresponding HFE's[a]

R/R′	k_{OH}(RR′)	k_{OH}(ROR′)	k_{Cl}(RR′)	k_{Cl}(ROR′)
CH_3/CH_3	2.4	25[b]	570	176[c]
CF_3/CH_3	0.012	0.12	0.0002	
CF_2H/CF_2H	0.057	0.023	0.022	0.573[d]
CF_2H/CF_3	0.019	0.004	0.002	

[a] Room-temperature rates in 10^{-13} cm^3 molecule^{-1} s^{-1}, from ref 9. [b] Reference 14. [c] Reference 15. [d] This work.

moiety. This is clearly demonstrated by comparing the reactivities of $CF_3CH_2OCH_3$ and $C_4F_9OCH_3$.

The C−H bond strengths of the HFE's under study were theoretically determined by performing ab initio calculations with the GAMESS programs package.[17] Calculations were performed for all molecules studied, CHF_2OCHF_2, $CF_3CH_2OCH_3$, $CF_3CH_2OCHF_2$, and $CF_3CH_2OCH_2CF_3$. Three different basis sets were employed (3-21G, 6-31G, and 6-311G where possible), augmented by one or two sets of polarization functions on d and/or p orbitals. Calculations were also performed with the addition of diffuse functions on s and/or p orbitals, on all atoms. Restricted Hartree−Fock wave functions (SCF-RHF) were used for all closed-shell species, while unrestricted wave functions (SCF-UHF) were used for the radical species. Electron correlation of the valence electrons was taken into account by second-order Møller−Plesset perturbation theory (MP2, frozen core). The geometry of the closed-shell species CHF_2OCHF_2 and $CF_3CH_2OCH_3$ was fully optimized and their vibrational frequencies were calculated at the MP2/3-21++G(2d,2p) and the MP2/3-21G levels of theory, respectively, while those of $CF_3CH_2OCHF_2$ and $CF_3CH_2OCH_2CF_3$ molecules were calculated at the RHF/3-21+G(2d) level. The corresponding calculations of the CHF_2OCF_2, $CF_3CH_2OCH_2$, and CF_3CHOCH_3 radicals were performed at the UHF/3-21++G(2d,2p) level of theory, while those for the $CF_3CH_2OCF_2$, $CF_3CHOCHF_2$, and $CF_3CH_2OCHCF_3$ radicals were performed at the UHF/3-21+G(2d) level. All vibrational frequencies calculated were scaled down by the factor 0.89, in order to take anharmonicity effects into account.[18] Single-point energy calculations were performed at three higher levels of theory (MP2/6-31G(d), MP2/6-31+G(d), and MP2/6-31+G(d,p)) for all species. Finally, single-point energy calculations at the MP2/6-31++G(2d,2p) and MP2/6-311++G(2d,2p) levels were performed only for the molecules CHF_2OCHF_2 and $CF_3CH_2OCH_3$, as well as for their singly dehydrogenated radicals; our computational resources limit the application of the latter high-quality basis sets to the smaller members of HFE's under consideration. The total enthalpy of every species was calculated at 298.15 K, by assuming the rigid rotor and harmonic oscillator approximations, and the C−H bond strengths derived are presented in Table 7. The calculated values for the C−H bond strengths are increasing with the complexity of the 6-31G basis set, while the corresponding values at the triple-ζ quality 6-311G basis set are slightly lower. However, for comparison purposes between the strengths of the entire variety of C−H bonds, the results with the more flexible 6-31+G(d,p) basis set will be employed.

The correlation of the bond strengths with the degree and position of fluorination in fluorinated ethers reflects an interplay between two electronic effects: (a) the strengthening of the C−H bonds due to the electron-withdrawing inductive effects of fluorine and/or oxygen atoms through σ-bonds, and (b) the weakening of the C(F,O)−H bonds due to the ability of fluorine or oxygen atoms to transfer π-electron density from their filled lone pairs to the carbon atom connected.

TABLE 7: C−H Bond Strengths (in kJ mol^{-1}) at 298.15 K of the Fluorinated Ethers Studied, Calculated at the MP2/6-31G(d), MP2/6-31+G(d), and MP2/6-31+G(d,p) Levels of Theory[a]

bond	MP2/6-31G(d)	MP2/6-31+G(d)	MP2/6-31+G(d,p)	MP2/6-31++G(2d,2p)	MP2/6-311++G(2d,2p)
CHF_2OCF_2−H	383.51	385.07	404.75	413.01	408.06
$CF_3CH_2OCH_2$−H	371.30	370.39	390.42	393.22	390.71
CF_3CH(−H)OCH_3	366.67	367.47	387.54	388.79	386.60
$CF_3CH_2OCF_2$−H	391.77	392.82	414.09		
CF_3CH(−H)$OCHF_2$	379.58	381.21	401.56		
CF3CH2OCH(−H)CF3	380.86	382.47	402.94		

[a] Calculations at the higher MP2/6-31++G(2d,2p) and MP2/6-311++G(2d,2p) levels were performed only for CHF_2OCHF_2 and $CF_3CH_2OCH_3$ molecules.

Among the fluoroethers studied, three main types of C−H bonds can be found, namely, $-OCF_2$−H, −OCH(CF_3)−H, and $-OCH_2$−H. An examination of the calculated C−H bond strengths in Table 7 shows that the $-OCF_2$−H bonds are the strongest, 404.75 and 414.09 kJ mol^{-1} for CHF_2OCF_2−H and $CF_3CH_2OCF_2$−H, respectively. The high strength of these C−H bonds is due to the combined electron-withdrawing inductive effects of two fluorine atoms and one oxygen atom adjacent to the hydrogen atom, which effectively compensate for the electron-donating conjugative effect of the oxygen atom. A comparison among the strengths of these C−H bonds indicates that the electron-withdrawing inductive effects of the CF_3CH_2O− group are probably more effective than those of the CHF_2O− group. For the second type of C−H bonds, the strengths of the $CF_3CH(OCH_3)$−H, $CF_3CH(OCHF_2)$−H, and $CF_3CH(OCH_2CF_3)$−H bonds are calculated to be 387.54, 401.56, and 402.94 kJ mol^{-1}, respectively. In this case, the inductive effects of the more distant fluorine atoms are not able to compensate efficiently the conjugative effects of the adjacent oxygen atom in the C−H bond strength. The lowest strength of the $CF_3CH(OCH_3)$−H bond compared to the $CF_3CH(OCHF_2)$−H bond can be explained by considering the higher negative inductive effects of the CHF_2O− group, compared to the CH_3O− group. The highest strength for the $CF_3CH(OCH_2CF_3)$−H bond is also supporting the above indication on the relative strengths of the inductive effects of the CF_3CH_2O− and CHF_2O− groups. The strength of the relatively weaker type of C−H bonds, $CF_3CH_2OCH_2$−H, has been calculated to be 390.42 kJ mol^{-1}. However, a comparison with the $CF_3CH(OCH_3)$−H bond shows that the latter is even weaker by ca. 3 kJ mol^{-1}; this is a surprising result, considering the relative distances of the C−H bond from the electron-withdrawing fluorine atoms. A similar result was obtained for all basis sets employed, showing that this is not an artifact of our electronic energy calculations. Therefore, the theoretical predictions favor the abstraction of the hydrogen atoms of the methylene group in $CF_3CH_2OCH_3$ and $CF_3CH_2OCHF_2$, by considering bond strengths alone.

A qualitative correlation of the observed rate constants and activation energies with the corresponding C−H bond strengths can now be drawn from the above results, within the contexts of the conventional transition state theory and the linear free-energy relationships (LFER). The rate constant and the absence of any significant activation energy of the fast reaction of $CF_3CH_2OCH_3$ with Cl correlate well with the corresponding low C−H bond strengths, 387.54 and 390.42 kJ mol^{-1}, for the secondary and primary hydrogen atoms, respectively. However, the abstraction of the methyl hydrogen atom should lead to a higher preexponential factor, considering the higher entropy of the corresponding transition state, due to the larger external moments of inertia of $[CF_3CH_2OCH_2\cdots H\cdots Cl]^‡$, compared to $[CF_3CH(\cdots H\cdots Cl)OCH_3]^‡$ transition state configuration. In addition, by taking into account the small difference of their corresponding bond strengths, the abstraction of the hydrogen atom of the methyl group is more likely to occur. The rate parameters for the slower reactions of the symmetrical molecules $CF_3CH_2OCH_2CF_3$ and CHF_2OCHF_2 with Cl are also correlating qualitatively well with the corresponding C−H bond strengths of 402.94 and 404.75 kJ mol^{-1}, respectively. For the slowest reaction of $CF_3CH_2OCHF_2$ with Cl, the high activation energy is in contrast with the relatively low C−H bond strength of the secondary hydrogen atom (most likely to be transferred on thermochemical grounds). By considering that the molecule consists of the groups $-CHF_2$ and $-CH_2CF_3$ connected to an oxygen atom, its rate constant with Cl should lie between the corresponding rate constants for the symmetrical CHF_2OCHF_2 and $CF_3CH_2OCH_2CF_3$ molecules. However, the activation energy and the rate constant measured are complex functions of the corresponding strengths of the bonds broken or formed and, furthermore, they include entropic factors, which are totally ignored when the rate parameters are correlated simply with bond strengths. In the case of the reaction of $CF_3CH_2OCHF_2$ with Cl atoms, there are two possibilities for Cl atoms approach: (a) to the hydrogen atoms of the methylene group, which, although thermochemically favored, results in a small transition state entropy, and (b) to the hydrogen atom of the $-CHF_2$ group, which, although thermochemically unfavored, leads to higher transition state entropy, mainly due to the resulting larger moments of inertia for the $[CF_3CH_2OCF_2\cdots H\cdots Cl]^‡$ transition state. However, the experimental results suggest that the $-OCF_2$−H hydrogen atom metathesis pathway is more likely to occur, manifested in the high value of the activation energy measured. In addition, the former competing pathway has probably a small contribution to the overall rate, due to its low preexponential factor and the corresponding low rate constant.

TABLE 8: Estimated Atmospheric Lifetimes (in years) of HFE's, CFC's and HCFC's[a]

species	τ_{OH}	τ_{Cl}	τ
HFE's			
CHF_2OCHF_2	13.90	61.60	11.30
$CF_3CH_2OCH_3$	0.05	0.14	0.04
$CF_3CH_2OCHF_2$	3.00	101.30	2.90
$CF_3CH_2OCH_2CF_3$	0.30	8.50	0.30
CFC's−HCFC's			
CF_3CH_2F			14.00
CF_2HCl			13.30
$CFCl_3$			50.00
CF_2Cl_2			102.00

[a] Rate constants for the reactions of HFE's with OH radicals were taken from refs 2 and 6.

In general, HFE's exhibit higher reactivity toward major tropospheric reactive species such as OH radicals and Cl atoms than CFC's and HCFC's, and therefore their tropospheric lifetimes will be sufficiently lower. An estimation of the atmospheric lifetimes of HFE's and commonly used CFC's and HCFC's is presented in Table 8, assuming average tropospheric concentrations of OH and Cl of 10^6 and 10^4 molecules cm^{-3}, respectively.[19]

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