

# Absolute Reaction Rates of Chlorine Atoms with CF<sub>3</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CH<sub>2</sub>FCH<sub>2</sub>OH

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The absolute rate constants for the reactions of chlorine atoms with a series of fluorinated ethanols CF<sub>3</sub>CH<sub>2</sub>OH (1), CHF<sub>2</sub>CH<sub>2</sub>OH (2), and CH<sub>2</sub>FCH<sub>2</sub>OH (3) were measured in the gas phase over the temperature range 273–363 K, by employing the discharge-flow mass spectrometric technique with a Knudsen type reactor. The absolute rate constants are given by the following expressions (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 2σ uncertainties):  $k_1 = (0.85 \pm 0.19) \times 10^{-11} \exp((-792 \pm 74)/T)$ ,  $k_2 = (2.61 \pm 0.49) \times 10^{-11} \exp((-662 \pm 60)/T)$ , and  $k_3 = (7.57 \pm 0.98) \times 10^{-11} \exp((-408 \pm 40)/T)$ . The title reactions take place primarily via the abstraction of methylene hydrogen, yielding the corresponding fluoroethanol radicals, which subsequently may undergo oxidation reactions, resulting in fluoroacetaldehydes. Quantum mechanical calculations of the C–H bond energies in the title alcohols at the B3P86/6-311++G(2df,p) level of theory show that the methylene hydrogen bonds are the weakest. The atmospheric degradation mechanism of the title fluorinated ethanols is also presented.

## Introduction

Fluoro alcohols (FAs) are proposed as a new generation of CFC alternatives,<sup>1,2</sup> since they do not contain chlorine or bromine atoms and are expected to be more reactive in the troposphere, in accordance with the Montreal protocol.<sup>3</sup> The tropospheric degradation of fluoro alcohols will primarily occur via reaction with OH radicals,<sup>4</sup> with a significant contribution from the reaction with the less abundant but more reactive Cl atoms. In particular, Cl atom reactions with hydrocarbons are important over coastal atmospheric environments,<sup>5–8</sup> where their concentration may be substantial (10<sup>4</sup> molecule cm<sup>-3</sup>),<sup>9</sup> or over urban environments by promoting the formation of tropospheric ozone.<sup>6,7,10</sup> Thus, the reactivity of FAs toward chlorine atoms should be examined in order to assist in a more accurate estimation of their atmospheric lifetimes and fully assess their potential impact on global warming and urban pollution problems. Furthermore, it is important to understand the reactivity of the C–H bonds in fluoro alcohols upon fluorination, by selecting the series of fluorinated ethanols CF<sub>3</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CH<sub>2</sub>FCH<sub>2</sub>OH.

Thus, the absolute rate constants for the reactions of chlorine atoms with the fluorinated ethanols CF<sub>3</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CH<sub>2</sub>FCH<sub>2</sub>OH were measured over the temperature range 273–363 K, by employing the discharge-flow mass spectrometric technique with a Knudsen type reactor. Furthermore, the chlorine atom-initiated oxidation of the title FAs was also investigated in order to elucidate their atmospheric degradation mechanism.

## Experimental Section

The title reactions were studied by using a discharge-flow mass spectrometric system equipped with a very low-pressure

reactor (VLPR), which has been described previously.<sup>11</sup> In brief, the reaction takes place in a cylindrical Knudsen type 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 signals are distinguished and amplified by a lock-in amplifier and are consequently stored and analyzed by a microcomputer.

The cylindrical reactors ( $V_1 = 298.3$  cm<sup>3</sup> and  $V_2 = 109$  cm<sup>3</sup>) were thermostated and coated with a thin Teflon film to inhibit wall reactions. The escape constants of all species from the reactor were determined by monitoring the first-order decay of their mass spectrometric signals after a fast halt of the flow, and they are given by the expression  $k_{\text{esc},M} = A_{\text{esc}}(T/M)^{1/2}$  s<sup>-1</sup>, where  $T$  is the temperature and  $M$  is the molecular weight. The coefficients  $A_{\text{esc}}$  were determined by plotting  $k_{\text{esc},M}$  versus  $(T/M)^{1/2}$  for several gases; for reactors with  $V_1$  and  $V_2$  with an escape aperture of 5 mm the,  $A_{\text{esc}}$  values were 0.996 and 2.661, respectively. The residence times ( $1/k_{\text{esc},M}$ ) of Cl atoms and FAs were 340 and 577 ms for the reactor with  $V_1$ , as well as 130 and 195 ms for the reactor with  $V_2$ , respectively. The flow rates of both reactants (through a 1 mm × 100 cm capillary) were determined by monitoring the pressure drop in a known volume at intervals of 2 min in a period of several hours.

Chlorine atoms were produced by flowing a mixture of 5% Cl<sub>2</sub> in He through a quartz tube enclosed in a 2.45 GHz microwave cavity operating at 35 W. The quartz tube was coated with a dried slush mixture of phosphoric and boric acids to inhibit Cl atoms' recombination. The decomposition of Cl<sub>2</sub> was complete (ca. 99%), and this was continually verified by the absence of the  $m/e = 70$  parent peak. The steady-state concentration of Cl atoms was determined by monitoring the

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**TABLE 1: Fragmentation Mass Spectra of CF<sub>3</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CH<sub>2</sub>FCH<sub>2</sub>OH Taken with 19 eV Electron Energy<sup>a</sup>**

CF <sub>3</sub> CH <sub>2</sub> OH								
<i>m/e</i>	29	31	51	69	83	99	100	
fragment	CHO <sup>+</sup>	M-CF <sub>3</sub> <sup>+</sup>	HCF <sub>2</sub> <sup>+</sup>	CF <sub>3</sub> <sup>+</sup>	M-OH <sup>+</sup>	M-H <sup>+</sup>	M <sup>+</sup>	
relative intensity	1	100	1	2	1	1	3	
CHF <sub>2</sub> CH <sub>2</sub> OH								
<i>m/e</i>	29	31	44	45	61	64	82	
fragment	CHO <sup>+</sup>	M-CHF <sub>2</sub> <sup>+</sup>	C <sub>2</sub> FH <sup>+</sup>	C <sub>2</sub> FH <sub>2</sub> <sup>+</sup>	C <sub>2</sub> HFO <sup>+</sup>	M-H <sub>2</sub> O <sup>+</sup>	M <sup>+</sup>	
relative intensity	1.4	100	2	1	1	1.5	4	
CH <sub>2</sub> FCH <sub>2</sub> OH								
<i>m/e</i>	29	31	33	44	45	46	63	64
fragment	CHO <sup>+</sup>	M-CH <sub>2</sub> F <sup>+</sup>	CH <sub>2</sub> F <sup>+</sup>	C <sub>2</sub> FH	C <sub>2</sub> FH <sub>2</sub> <sup>+</sup>	M-H <sub>2</sub> O <sup>+</sup>	M-H <sup>+</sup>	M <sup>+</sup>
relative intensity	2	100	1	2	1	2	1	22

<sup>a</sup> Intensities are reported relative to the intensity of the most prominent mass peak, where M is the parent molecule.

**TABLE 2: Typical Experimental Data for the Steady-State Concentrations of Cl Atoms and CH<sub>2</sub>FCH<sub>2</sub>OH Molecules, and  $(R - 1)k_{\text{esc,Cl}}$  (in s<sup>-1</sup>)<sup>a</sup>**

[Cl] <sub>0</sub>	[Cl]	[CH <sub>2</sub> FCH <sub>2</sub> OH] <sub>0</sub>	[CH <sub>2</sub> FCH <sub>2</sub> OH]	$(R - 1)k_{\text{esc,Cl}}$
<i>T</i> = 273 K				
13.40	11.94	2.79	0.55	1.10
11.83	6.48	10.24	3.58	6.12
11.56	5.37	12.92	5.67	8.56
11.70	4.28	16.04	8.15	12.89
14.66	4.20	19.37	11.54	18.53
<i>T</i> = 303 K				
15.5	10.72	6.65	1.06	3.51
14.6	6.75	14.67	4.39	9.12
14.8	5.53	18.83	6.79	13.12
12.93	3.97	16.85	8.76	17.66
13.09	3.39	20.62	11.77	22.39
<i>T</i> = 333 K				
12.71	9.24	6.02	0.92	3.08
9.64	4.78	10.31	4.09	8.34
11.08	4.35	12.97	5.77	12.68
10.72	3.16	18.98	9.56	19.60
18.26	3.77	30.71	13.69	31.52
<i>T</i> = 363 K				
13.39	10.14	5.46	0.75	2.74
7.82	4.90	5.80	1.50	5.09
10.75	6.18	6.91	2.54	5.50
10.64	4.36	15.45	4.97	12.36
10.83	3.61	19.89	7.08	17.15

<sup>a</sup>  $R = ([\text{Cl}]_0/[\text{Cl}])$ . The subscript 0 denotes the steady-state concentration in the absence of the other reactant. All concentrations are expressed in units of 10<sup>11</sup> molecule cm<sup>-3</sup>.

mass peak at *m/e* = 35 with 19 eV electron energy, in which the contribution of HCl fragmentation is negligible (ca. 0.3%).

The stated purities of all fluoro alcohols were as follows: CF<sub>3</sub>CH<sub>2</sub>OH (99.5%+, Aldrich), CHF<sub>2</sub>CH<sub>2</sub>OH (95%, Fluorochem), and CH<sub>2</sub>FCH<sub>2</sub>OH (95%, Aldrich). However, their purities were further tested by GC/MS and NMR analysis, which showed that CF<sub>3</sub>CH<sub>2</sub>OH did not contain any impurity, CH<sub>2</sub>FCH<sub>2</sub>OH impurities were negligible, and CHF<sub>2</sub>CH<sub>2</sub>OH contained mainly (ca. 3%) HC≡CF (*m/e* = 44). Fluoroethyne, HC≡CF, was removed from CHF<sub>2</sub>CH<sub>2</sub>OH by fractional distillation at 77 K. The fragmentation mass spectra of the title FAs were taken with 19 eV electron energy and are shown in Table 1. The steady-state concentration of FAs was determined by monitoring their parent peaks at *m/e* = 100, 82, and 64 for CF<sub>3</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CH<sub>2</sub>FCH<sub>2</sub>OH, respectively, which did not have any contribution from reaction products.

The mass spectrometric signal intensity *I<sub>M</sub>* was given by the expression  $I_M = \alpha_M F_M = \alpha_M k_{\text{esc,M}} V [M]$ , where  $\alpha_M$  is a mass spectrometric calibration factor, *F<sub>M</sub>* is the flow rate, *V* is the reactor volume, and  $k_{\text{esc,M}}$  is the escape constant. The  $\alpha_M$  factors for FAs were determined from accurate calibration curves, by

**TABLE 3: Typical Experimental Data for the Steady-State Concentrations of Cl Atoms and CHF<sub>2</sub>CH<sub>2</sub>OH Molecules, and  $(R - 1)k_{\text{esc,Cl}}$  (in s<sup>-1</sup>)<sup>a</sup>**

[Cl] <sub>0</sub>	[Cl]	[CHF <sub>2</sub> CH <sub>2</sub> OH] <sub>0</sub>	[CHF <sub>2</sub> CH <sub>2</sub> OH]	$(R - 1)k_{\text{esc,Cl}}$
<i>T</i> = 273 K				
23.48	17.07	18.52	12.42	2.79
22.88	9.93	55.09	41.14	9.69
23.25	8.47	71.98	55.53	12.97
23.24	6.95	118.92	95.49	24.23
17.91	3.62	136.65	124.50	29.28
<i>T</i> = 303 K				
17.25	14.99	17.25	11.30	3.22
18.31	7.94	44.62	33.95	10.22
19.02	6.47	69.84	55.60	15.18
19.20	5.54	82.14	71.16	19.28
19.15	3.91	110.70	98.04	30.51
<i>T</i> = 333 K				
14.65	7.73	28.91	20.50	7.35
14.10	5.93	45.34	30.00	11.29
14.30	4.55	66.88	49.26	17.58
18.96	5.66	77.26	52.17	19.30
19.35	5.14	92.40	66.00	22.70
<i>T</i> = 363 K				
11.26	9.69	7.44	4.75	1.40
11.64	6.44	29.90	17.62	6.91
11.60	4.89	45.24	29.07	11.74
8.30	2.67	57.96	42.06	18.12
12.70	3.40	88.64	53.84	23.42

<sup>a</sup>  $R = ([\text{Cl}]_0/[\text{Cl}])$ . The subscript 0 denotes the steady-state concentration in the absence of the other reactant. All concentrations are expressed in units of 10<sup>11</sup> molecule cm<sup>-3</sup>.

plotting *I<sub>M</sub>* versus *F<sub>M</sub>*. The concentration ranges of reactants were as follows: [Cl] = (0.1–2) × 10<sup>12</sup> molecule cm<sup>-3</sup>, [CF<sub>3</sub>CH<sub>2</sub>OH] = (6.5 × 10<sup>11</sup> to 2.5 × 10<sup>13</sup>) molecule cm<sup>-3</sup>, [CHF<sub>2</sub>CH<sub>2</sub>OH] = (2.2 × 10<sup>11</sup> to 1.4 × 10<sup>13</sup>) molecule cm<sup>-3</sup>, and [CH<sub>2</sub>FCH<sub>2</sub>OH] = (4.1 × 10<sup>10</sup> to 2.1 × 10<sup>12</sup>) molecule cm<sup>-3</sup>. In the oxidation experiments the O<sub>2</sub> concentration was in the range (0.1–1) × 10<sup>14</sup> molecule cm<sup>-3</sup>. The uncertainty in the mass spectral intensity measurements was ~5%; thus, the accuracy in the determination of  $[Cl]_0/[Cl] = I_{Cl,0}/I_{Cl}$  was ~7%.

## Results

Mass spectrometric analysis of the reaction products showed that HCl (*m/e* = 36) was the primary reaction product. Typical experimental data from all three reactions are presented in Tables 2–4, showing very good mass balance for reactants ( $\Delta[Cl]k_{\text{esc,Cl}} = \Delta[FA]k_{\text{esc,FA}}$ ) within experimental error. For the slowest reaction (1) the rate constants were also derived by assuming the pseudo-first-order conditions ( $[CH_2FCH_2OH] \cong [CH_2FCH_2OH]_0$ ), and these rates were equal within 5%, with the values obtained by monitoring the concentration of both reactants.

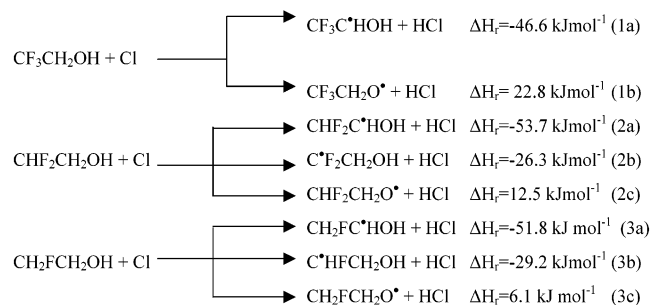
**TABLE 4: Typical Experimental Data for the Steady-State Concentrations of Cl Atoms and CF<sub>3</sub>CH<sub>2</sub>OH Molecules, and (R - 1)k<sub>esc,Cl</sub> (in s<sup>-1</sup>)<sup>a</sup>**

[Cl] <sub>0</sub>	[Cl]	[CF <sub>3</sub> CH <sub>2</sub> OH] <sub>0</sub>	[CF <sub>3</sub> CH <sub>2</sub> OH]	(R - 1)k <sub>esc,Cl</sub>
T = 273 K				
17.96	11.35	48.28	27.32	1.29
18.12	9.61	65.65	43.77	1.97
18.13	7.82	90.77	64.06	2.93
10.44	4.08	96.16	88.16	4.38
17.96	5.86	139.48	105.38	4.59
T = 303 K				
22.10	13.88	42.73	22.98	1.39
21.65	8.19	93.52	58.87	3.85
18.75	6.64	120.69	85.06	5.40
15.72	3.96	147.63	121.00	8.81
17.84	3.90	209.54	172.64	10.61
T = 333 K				
12.92	7.63	33.29	24.99	2.16
11.85	6.14	50.86	40.84	2.90
12.07	3.75	112.76	90.10	6.88
11.27	2.14	197.04	166.94	13.31
11.16	1.84	225.73	212.45	15.74
T = 363 K				
11.68	8.42	34.25	31.10	3.32
11.75	7.53	56.07	46.89	4.80
11.59	6.40	83.85	72.73	6.96
11.28	5.53	105.09	89.77	8.91
11.42	5.28	128.30	110.72	9.95

<sup>a</sup> R = ([Cl]<sub>0</sub>/[Cl]). The subscript 0 denotes the steady-state concentration in the absence of the other reactant. All concentrations are expressed in units of 10<sup>11</sup> molecule cm<sup>-3</sup>.

Moreover, the correlation between Cl atoms and HCl was excellent within experimental error (the ratio of their calibration factors α<sub>HCl</sub>/α<sub>Cl</sub> was 1.1 ± 0.1 for 19 eV electron energy<sup>12</sup>). The total pressure in the reactor was in the range 1–3 mTorr, to avoid secondary reactions.

Thus, the reactions may occur via the following hydrogen transfer pathways:

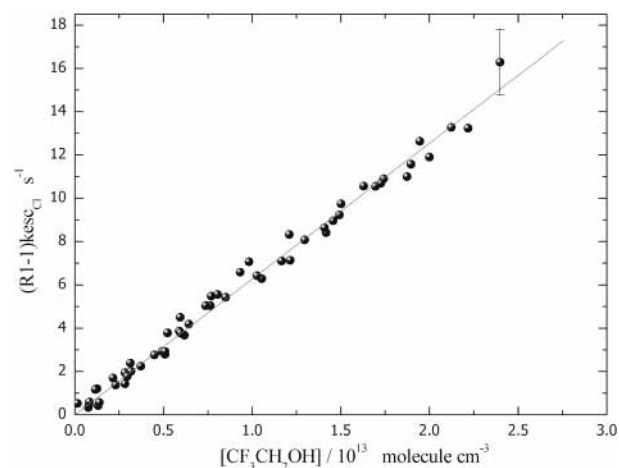


The reaction enthalpies were obtained by performing theoretical calculations using the B3P86 density functional, which are discussed below.

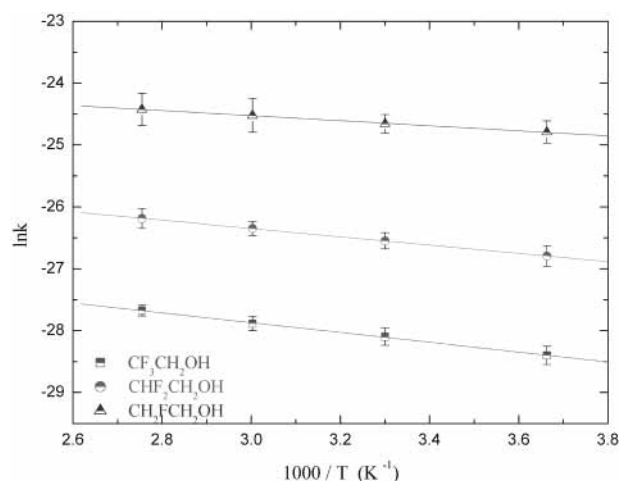
Application of a steady-state approximation for Cl atoms leads to the expression Δ[Cl]k<sub>esc,Cl</sub> = k[Cl][FA], where Δ[Cl] is the steady-state concentration difference [Cl]<sub>0</sub> - [Cl]<sub>r</sub> (the subscripts 0 and r denote the absence or presence of FA reactant, respectively), k<sub>esc,Cl</sub> is the escape rate of Cl atoms, k is the total rate constant, and [FA] is the steady-state concentration of the FA reactant. By rearrangement, the above expression becomes

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

where R = [Cl]<sub>0</sub>/[Cl]<sub>r</sub> = I<sub>35,0</sub>/I<sub>35,r</sub>. Therefore, the rate constants were determined by monitoring the ratio R at different FA steady concentrations, and a typical plot of the above expression for



**Figure 1.** Plot of (R - 1)k<sub>esc,Cl</sub> versus [CF<sub>3</sub>CH<sub>2</sub>OH] at 303 K. The error bar reflects the propagated errors (2σ).



**Figure 2.** Arrhenius plots of k<sub>Cl</sub> versus 1000/T for all three reactions. Error bars reflect the total propagated errors (2σ).

**TABLE 5: Rate Constants of the Title Reactions (in 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 2σ Uncertainty) at the Temperatures 273, 303, 333, and 363 K**

FA	273 K	303 K	333 K	363 K
CF <sub>3</sub> CH <sub>2</sub> OH	0.46 ± 0.07	0.63 ± 0.09	0.78 ± 0.09	0.96 ± 0.09
CHF <sub>2</sub> CH <sub>2</sub> OH	2.31 ± 0.38	2.95 ± 0.39	3.61 ± 0.41	4.24 ± 0.69
CH <sub>2</sub> FCH <sub>2</sub> OH	17.1 ± 3.1	19.6 ± 2.9	22.4 ± 6.1	24.7 ± 6.4

**TABLE 6: Rate Parameters for the Reactions of Cl Atoms with FAs (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, 2σ Uncertainty)**

FA	10 <sup>-12</sup> k <sub>298</sub>	10 <sup>-11</sup> A	E <sub>a</sub> /R
CF <sub>3</sub> CH <sub>2</sub> OH	0.63 ± 0.09	0.85 ± 0.19	792 ± 74
CHF <sub>2</sub> CH <sub>2</sub> OH	2.95 ± 0.39	2.61 ± 0.49	662 ± 60
CH <sub>2</sub> FCH <sub>2</sub> OH	19.6 ± 2.9	7.57 ± 0.98	408 ± 40

reaction 1 is presented in Figure 1. The linear least-squares fit to the data yields the rate constant k with a precision ~10% (2σ).

The rate constants for all FAs were determined at four different temperatures, 273, 303, 333, and 363 K, and the values obtained are listed in Table 5. Linear least-squares analysis of the temperature dependence data yields the activation energies and the A-factors for all reactions, which are given in Table 6. Finally, the Arrhenius plots of the title reactions are presented in Figure 2.

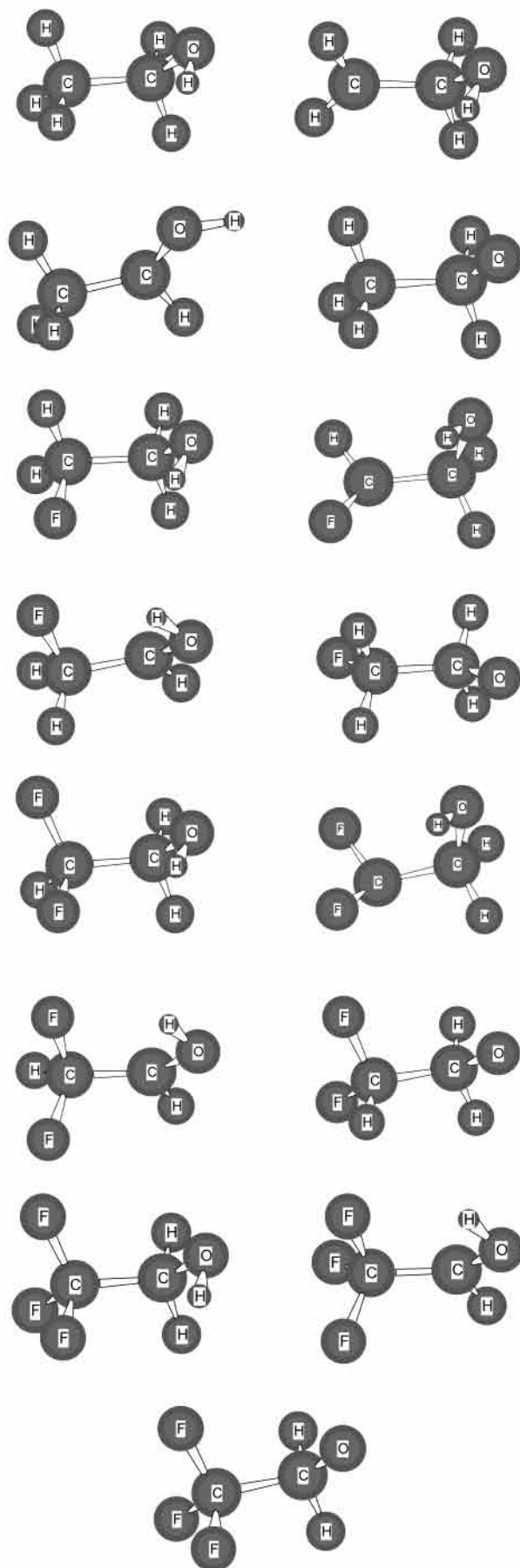
Experiments were also performed with the addition of O<sub>2</sub> in the reactor (through a third inlet), to study the primary oxidation process of the resulting fluoroethanol radicals and investigate

the reaction mechanism of the title reactions. The sole oxidation products were the corresponding fluoroacetaldehydes, namely  $\text{CF}_3\text{C(H)O}$  ( $m/e = 98, 69,$  and  $29$ ) for reaction 1,  $\text{CHF}_2\text{C(H)O}$  ( $m/e = 80, 51,$  and  $29$ ) for reaction 2, and  $\text{CH}_2\text{FC(H)O}$  ( $m/e = 62, 33,$  and  $29$ ) for reaction 3. Their yields were proportional to the FAs concentrations, suggesting that the oxidation reactions occur via hydrogen abstraction from the corresponding fluoroethanol radicals. Considering that the reaction of Cl atom with ethanol proceeds predominantly via hydrogen abstraction from the  $\text{CH}_2$  group ( $\approx 93\%$ ) and to a much lesser extent from the  $\text{CH}_3$  and OH groups,<sup>20</sup> similar behavior is expected for the title FAs. Thus, the oxidation reactions should occur predominantly via the following reactions:



### Theoretical Calculations

To provide a better understanding of the primary reaction pathways, the C–H and O–H bond strengths of  $\text{CH}_2\text{FCH}_2\text{OH}$ ,  $\text{CHF}_2\text{CH}_2\text{OH}$ , and  $\text{CF}_3\text{CH}_2\text{OH}$ , as well as those of  $\text{CH}_3\text{OH}$ ,  $\text{CF}_3\text{OH}$ , and  $\text{CH}_3\text{CH}_2\text{OH}$  that were used as benchmark molecules, were calculated at the B3P86/6-311++G(2df,p) and B3P86/6-311++G(3df,2p) levels of theory, which have been shown to predict accurate bond dissociation energies.<sup>13</sup> The calculations were performed by the Gaussian 94 program suite.<sup>14</sup> Restricted Hartree–Fock (RHF) wave functions were used for all closed shell species, and unrestricted Hartree–Fock (UHF) wave functions were used for the free radical species. The structural parameters and the vibrational frequencies of all species were calculated at the B3P86/6-31G(d) level of theory, which was found to be sufficiently accurate for the calculation of molecular structures.<sup>13</sup> A systematic conformational analysis was performed for all parent alcohols and their corresponding singly dehydrogenated radicals, since the energetic differences of various conformers calculated at the B3P86/6-31G(d), B3P86/6-311++G(2df,p), B3P86/6-311++G(3df,2p), and MP2/6-311G(d) levels of theory were found to exceed  $10 \text{ kJ mol}^{-1}$  in some cases. The more stable conformers were generally characterized by the tendency of the hydroxyl hydrogen atom to approach fluorine atoms, and thus in all cases except the  $\text{CH}_3\text{-CHOH}$  radical, it is oriented toward the C–C bond. The optimized structures are depicted in Figure 3, and their structural parameters are presented in Table 7. They were verified to be true potential energy minima by the absence of imaginary vibrational frequencies. Subsequently, single-point energies were calculated at the B3P86/6-311++G(2df,p) and B3P86/6-311++G(3df,2p) levels of theory, and the enthalpies of the bond dissociation reactions,  $\text{R-H} \rightarrow \text{R} + \text{H}$ , were calculated at 298.15 K by adding the zero-point energies and the thermal corrections to the total enthalpy, assuming the harmonic oscillator and rigid rotor approximations. All vibrational frequencies were scaled down by the factor 0.9723 in order to compensate for the overestimation of the harmonic frequencies at the B3P86/6-31G(d) level of theory.<sup>13</sup> The C–H and O–H bond dissociation enthalpies at 298.15 K for  $\text{CH}_3\text{OH}$ ,  $\text{CF}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , and the fluorinated alcohols  $\text{CH}_2\text{FCH}_2\text{OH}$ ,  $\text{CHF}_2\text{CH}_2\text{OH}$ , and  $\text{CF}_3\text{-CH}_2\text{OH}$  calculated at the B3P86/6-311++G(2df,p) and B3P86/6-311++G(3df,2p) levels of theory are listed in Table 8, along with the experimental values obtained from the available



**Figure 3.** Structures for  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CF}_3\text{CH}_2\text{OH}$ ,  $\text{CHF}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{-FCH}_2\text{OH}$ , and the corresponding radical products calculated at the B3P86/6-31G(d) level of theory.



**TABLE 7: Structural Parameters of CH<sub>3</sub>OH, CF<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>2</sub>FCH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CF<sub>3</sub>CH<sub>2</sub>OH as Well of Their Singly Dehydrogenated Radicals, Optimized at the B3P86/6-31G(d) Level of Theory (Bond Lengths in Å, Angles in Degrees)**

CH <sub>3</sub> OH	C-O	1.410	H1-O	0.966	C-H2	1.093	C-H3	1.101
	C-H4	1.101						
	∠H1-O-C	107.66	∠H2-C-O	106.78	∠H3-C-O	112.80	∠H4-C-O	112.80
	∠H2-C(-O)-H1	180.00	∠H3-C(-O)-H2	118.42	∠H4-C(-O)-H3	123.17		
CH <sub>3</sub> O	C-O	1.361	C-H1	1.103	C-H2	1.103	C-H3	1.110
	∠H1-C-O	113.68	∠H2-C-O	113.68	∠H3-C-O	105.19		
	∠H2-C(-O)-H1	128.31	∠H3-C(-O)-H2	115.84				
	C-H1	1.083	C-H2	1.088	C-O	1.364	H3-O	0.967
CH <sub>2</sub> OH	∠H2-C-H1	119.82	∠O-C-H2	118.67	∠H3-O-C	108.83		
	∠O-C(-H2)-H1	214.74	∠H3-O(-C)-H2	331.10				
	C-O	1.346	H-O	0.969	C-F1	1.325	C-F2	1.345
	C-F3	1.345						
CF <sub>3</sub> OH	∠H-O-C	108.60	∠F1-C-O	108.34	∠F2-C-O	112.17	∠F3-C-O	112.17
	∠F1-C(-O)-H	180.00	∠F2-C(-O)-F1	120.09	∠F3-C(-O)-F2	119.82		
	C-O	1.351	C-F1	1.332	C-F2	1.332	C-F3	1.337
	∠F1-C-O	112.39	∠F2-C-O	112.39	∠F3-C-O	104.94		
CF <sub>3</sub> O	∠F2-C(-O)-F1	121.64	∠F3-C(-O)-F2	119.18				
	O-C1	1.416	C2-C1	1.520	H1-C1	1.102	H2-C1	1.095
	H3-C2	1.097	H4-C2	1.094	H5-C2	1.096	H6-O	0.967
	∠C2-C1-O	112.85	∠H1-C1-C2	110.12	∠H2-C1-C2	110.18	∠H3-C2-C1	111.07
CH <sub>3</sub> CH <sub>2</sub> OH	∠H4-C2-C1	110.41	∠H5-C2-C1	111.10	∠H6-O-C1	107.35		
	∠H1-C1(-C2)-O	124.85	∠H2-C1(-C2)-H1	117.67	∠H3-C2(-C1)-H1	61.45	∠H4-C2(-C1)-H3	119.85
	∠H5-C2(-C1)-H4	120.53	∠H6-O(-C1)-C2	61.64				
	O-C1	1.364	C2-C1	1.546	H1-C1	1.104	H2-C1	1.104
	H3-C2	1.092	H4-C2	1.092	H5-C2	1.094		
	∠C2-C1-O	106.23	∠H1-C1-C2	108.19	∠H2-C1-C2	108.19	∠H3-C2-C1	110.26
	∠H4-C2-C1	110.26	∠H5-C2-C1	108.66				
	∠H1-C1(-C2)-O	120.69	∠H2-C1(-C2)-H1	118.62	∠H3-C2(-C1)-H1	60.43	∠H4-C2(-C1)-H3	120.52
	∠H5-C2(-C1)-H4	119.74						
CH <sub>3</sub> CHOH	O-C1	1.371	C2-C1	1.481	H1-C1	1.091	H2-C2	1.104
	H3-C2	1.097	H4-C2	1.094	H5-O	0.966		
	∠C2-C1-O	114.17	∠H1-C1-C2	120.40	∠H2-C2-C1	112.77	∠H3-C2-C1	110.68
	∠H4-C2-C1	110.34	∠H5-O-C1	108.68				
	∠H1-C1(-C2)-O	146.25	∠H2-C2(-C1)-H1	79.26	∠H3-C2(-C1)-H2	119.70	∠H4-C2(-C1)-H3	119.84
	∠H5-O(-C1)-C2	178.08						
CH <sub>2</sub> CH <sub>2</sub> OH	O-C1	1.419	C2-C1	1.483	H1-C1	1.103	H2-C1	1.102
	H3-C2	1.085	H4-C2	1.086	H5-O	0.968		
	∠C2-C1-O	112.96	∠H1-C1-C2	110.19	∠H2-C1-C2	111.18	∠H3-C2-C1	121.32
	∠H4-C2-C1	119.30	∠H5-O-C1	106.66				
	∠H1-C1(-C2)-O	125.46	∠H2-C1(-C2)-H1	117.22	∠H3-C2(-C1)-H1	333.35	∠H4-C2(-C1)-H3	190.52
	∠H5-O(-C1)-C2	54.53						
CH <sub>2</sub> FCH <sub>2</sub> OH	O-C1	1.409	C2-C1	1.509	H1-C1	1.102	H2-C1	1.095
	H3-C2	1.095	H4-C2	1.096	C2-F	1.394	H5-O	0.969
	∠C2-C1-O	111.06	∠H1-C1-C2	109.12	∠H2-C1-C2	109.91	∠H3-C2-C1	110.80
	∠H4-C2-C1	112.05	∠F-C2-C1	107.70	∠H5-O-C1	105.82		
	∠H1-C1(-C2)-O	123.48	∠H2-C1(-C2)-H1	118.00	∠H3-C2(-C1)-H1	181.60	∠H4-C2(-C1)-H3	122.92
	∠F-C2(-C1)-H4	119.37	∠H5-O(-C1)-C2	52.69				
CH <sub>2</sub> FCH <sub>2</sub> O	O-C1	1.358	C2-C1	1.522	H1-C1	1.109	H2-C1	1.109
	H3-C2	1.096	H4-C2	1.096	C2-F	1.383		
	∠C2-C1-O	114.48	∠H1-C1-C2	110.51	∠H2-C1-C2	110.60	∠H3-C2-C1	110.40
	∠H4-C2-C1	110.49	∠F-C2-C1	108.73				
	∠H1-C1(-C2)-O	123.08	∠H2-C1(-C2)-H1	113.63	∠H3-C2(-C1)-H1	62.95	∠H4-C2(-C1)-H3	120.47
	∠F-C2(-C1)-H4	119.78						
CH <sub>2</sub> FCHOH	O-C1	1.359	C2-C1	1.477	H1-C1	1.083	H2-C2	1.095
	H3-C2	1.103	C2-F	1.403	H4-O	0.972		
	∠C2-C1-O	117.04	∠H1-C1-C2	121.78	∠H2-C2-C1	111.52	∠H3-C2-C1	113.48
	∠F-C2-C1	107.97	∠H4-O-C1	106.32				
	∠H1-C1(-C2)-O	148.36	∠H2-C2(-C1)-H1	316.09	∠H3-C2(-C1)-H2	123.08	∠F-C2(-C1)-H3	116.65
	∠H4-O(-C1)-C2	330.08						
CHFCH <sub>2</sub> OH	O-C1	1.428	C2-C1	1.479	H1-C1	1.101	H2-C1	1.093
	H3-C2	1.087	C2-F	1.349	H4-O	0.968		
	∠C2-C1-O	113.29	∠H1-C1-C2	109.37	∠H2-C1-C2	109.30	∠H3-C2-C1	123.53
	∠F-C2-C1	115.10	∠H4-O-C1	106.77				
	∠H1-C1(-C2)-O	124.41	∠H2-C1(-C2)-H1	118.00	∠H3-C2(-C1)-H1	194.83	∠F-C2(-C1)-H3	214.43
	∠H4-O(-C1)-C2	60.59						
CHF <sub>2</sub> CH <sub>2</sub> OH	O-C1	1.402	C2-C1	1.512	H1-C1	1.103	H2-C1	1.094
	H3-C2	1.096	F1-C2	1.373	F2-C2	1.355	H4-O	0.969
	∠C2-C1-O	111.83	∠H1-C1-C2	107.78	∠H2-C1-C2	109.21	∠H3-C2-C1	113.39
	∠F1-C2-C1	107.91	∠F2-C2-C1	111.17	∠H4-O-C1	106.72		
	∠H1-C1(-C2)-O	124.13	∠H2-C1(-C2)-H1	117.04	∠H3-C2(-C1)-H1	309.59	∠F1-C2(-C1)-H3	119.64
	∠F2-C2(-C1)-F1	117.56	∠H4-O(-C1)-C2	51.23				

**TABLE 7. (Continued)**

CHF <sub>2</sub> CH <sub>2</sub> O	O–C1	1.358	C2–C1	1.519	H1–C1	1.108	H2–C1	1.106
	H3–C2	1.095	F1–C2	1.357	F2–C2	1.363		
	∠C2–C1–O	114.27	∠H1–C1–C2	109.54	∠H2–C1–C2	109.56	∠H3–C2–C1	112.88
	∠F1–C2–C1	109.34	∠F2–C2–C1	108.65				
	∠H1–C1(–C2)–O	120.57	∠H2–C1(–C2)–H1	114.25	∠H3–C2(–C1)–H1	67.95	∠F1–C2(–C1)–H3	120.91
	∠F2–C2(–C1)–F1	117.95						
CHF <sub>2</sub> CHOH	O–C1	1.351	C2–C1	1.474	H1–C1	1.082	H2–C2	1.094
	F1–C2	1.377	F2–C2	1.378	H3–O	0.973		
	∠C2–C1–O	118.33	∠H1–C1–C2	121.88	∠H2–C2–C1	113.56	∠F1–C2–C1	113.18
	∠F2–C2–C1	107.75	∠H3–O–C1	107.10				
	∠H1–C1(–C2)–O	153.48	∠H2–C2(–C1)–H1	310.95	∠F1–C2(–C1)–H2	122.73	∠F2–C2(–C1)–F1	116.46
	∠H3–O(–C1)–C2	338.12						
CF <sub>2</sub> CH <sub>2</sub> OH	O–C1	1.417	C2–C1	1.495	H1–C1	1.099	H2–C1	1.092
	F1–C2	1.331	F2–C2	1.343	H3–O	0.968		
	∠C2–C1–O	112.91	∠H1–C1–C2	108.15	∠H2–C1–C2	108.78	∠F1–C2–C1	116.31
	∠F2–C2–C1	113.90	∠H3–O–C1	107.37				
	∠H1–C1(–C2)–O	124.55	∠H2–C1(–C2)–H1	117.39	∠F1–C2(–C1)–H1	190.85	∠F2–C2(–C1)–F1	230.56
	∠H3–O(–C1)–C2	62.26						
CF <sub>3</sub> CH <sub>2</sub> OH	O–C1	1.400	C2–C1	1.515	H1–C1	1.100	H2–C1	1.092
	F1–C2	1.352	F2–C2	1.337	F3–C2	1.344	H3–O	0.968
	∠C2–C1–O	111.90	∠H1–C1–C2	107.32	∠H2–C1–C2	108.42	∠F1–C2–C1	110.05
	∠F2–C2–C1	112.63	∠F3–C2–C1	110.65	∠H3–O–C1	107.62		
	∠H1–C1(–C2)–O	124.78	∠H2–C1(–C2)–H1	116.79	∠F1–C2(–C1)–H1	67.12	∠F2–C2(–C1)–F1	119.83
	∠F3–C2(–C1)–F2	121.14	∠H3–O(–C1)–C2	61.51				
CF <sub>3</sub> CH <sub>2</sub> O	O–C1	1.362	C2–C1	1.542	H1–C1	1.101	H2–C1	1.101
	F1–C2	1.334	F2–C2	1.334	F3–C2	1.341		
	∠C2–C1–O	108.54	∠H1–C1–C2	105.54	∠H2–C1–C2	105.54	∠F1–C2–C1	111.45
	∠F2–C2–C1	111.45	∠F3–C2–C1	108.54				
	∠H1–C1(–C2)–O	121.43	∠H2–C1(–C2)–H1	117.13	∠F1–C2(–C1)–H1	60.71	∠F2–C2(–C1)–F1	121.46
	∠F3–C2(–C1)–F2	119.27						
CF <sub>3</sub> CHOH	O–C1	1.349	C2–C1	1.477	H1–C1	1.081	F1–C2	1.354
	F2–C2	1.359	F3–C2	1.340	H2–O	0.972		
	∠C2–C1–O	118.74	∠H1–C1–C2	120.57	∠F1–C2–C1	114.45	∠F2–C2–C1	109.28
	∠F3–C2–C1	111.51	∠H2–O–C1	108.14				
	∠H1–C1(–C2)–O	152.80	∠F1–C2(–C1)–H1	69.00	∠F2–C2(–C1)–F1	118.65	∠F3–C2(–C1)–F2	120.15
	∠H2–O(–C1)–C2	336.14						

**TABLE 8: C–H and O–H Bond Strengths (in kJ mol<sup>-1</sup>) of CH<sub>3</sub>OH, CF<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>2</sub>FCH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CF<sub>3</sub>CH<sub>2</sub>OH at the B3P86/6-311++G(2df,p) and B3P86/6-311++G(3df,2p) Levels of Theory**

bond	exp value <sup>a</sup>	B3P86/6-311++	B3P86/6-311++
		G(2df,p)	G(3df,2p)
CH <sub>2</sub> OH–H	410.0 ± 4.0	401.1	401.2
CH <sub>3</sub> O–H	436.0 ± 4.0	430.0	432.4
CF <sub>3</sub> O–H	502.5 ± 15.8	494.6	496.4
CH <sub>2</sub> CH <sub>2</sub> OH–H	419.7 ± 8.4	424.5	424.4
CH <sub>3</sub> CHOH–H		390.7	391.0
CH <sub>3</sub> CH <sub>2</sub> O–H	436.0 ± 4.2	435.9	438.3
CHFCH <sub>2</sub> OH–H		416.3	415.2
CH <sub>2</sub> FCHOH–H		393.6	392.5
CH <sub>2</sub> FCH <sub>2</sub> O–H		450.1	450.5
CF <sub>2</sub> CH <sub>2</sub> OH–H		417.9	418.1
CHF <sub>2</sub> CHOH–H		390.2	390.7
CHF <sub>2</sub> CH <sub>2</sub> O–H		455.1	456.9
CF <sub>3</sub> CHOH–H		397.2	397.8
CF <sub>3</sub> CH <sub>2</sub> O–H		465.3	467.2

<sup>a</sup> Experimental bond strengths calculated from the corresponding enthalpies of formation (from ref 15, except for CH<sub>3</sub>OH, CH<sub>2</sub>OH, and CH<sub>3</sub>O, whose values were taken from ref 16).

corresponding enthalpies of formation.<sup>15,16</sup> The agreement between calculated and experimental bond strengths is excellent within ~5 kJ mol<sup>-1</sup>, suggesting that the levels of theory employed for the title fluorinated alcohols are very accurate. The variations calculated for the C–H bond strengths may be attributed to a combination of  $\sigma$ -type (inductive) and  $\pi$ -type (anomeric) effects, as presented elsewhere.<sup>17</sup> More specifically, the methyl C–H bond strengths can be arranged in the order H–CH<sub>2</sub>CH<sub>2</sub>OH > H–CF<sub>2</sub>CH<sub>2</sub>OH > H–CHFCH<sub>2</sub>OH, due to the combination of the anomeric effect of a fluorine atom, which

tends to stabilize the corresponding carbon-centered radical by the donation of  $\pi$ -type electron density, and the inductive effects of fluorine atoms, which tend to strengthen all neighboring bonds. Moreover, the inductive effect of a fluorine atom on an adjacent C–H bond appears to be weaker than its anomeric effect (as in the case of the CH<sub>3</sub>–H and CH<sub>2</sub>F–H bond strengths<sup>13,15</sup>), resulting in H–CHFCH<sub>2</sub>OH being the weakest bond. The methylene C–H bond strengths can be arranged in the order CF<sub>3</sub>CHOH–H > CH<sub>2</sub>FCHOH–H > CHF<sub>2</sub>CHOH–H > CH<sub>3</sub>–CHOH–H as a result of the inductive effects of fluorine atoms. In general, the methylene C–H bonds were calculated to be weaker than those of the methyl group by ~15 kJ mol<sup>-1</sup>, due to the strong anomeric effect of the oxygen atom. The unexpected result of the CH<sub>2</sub>FCHOH–H bond being stronger (by ~3 kJ mol<sup>-1</sup>) than the CHF<sub>2</sub>CHOH–H bond may be attributed to several factors, including intrinsic errors of the theoretical method employed and a varying extent of  $\pi$ -type orbitals' overlap due to variations of the OH group orientation. The strength of the O–H bonds was calculated to be the highest for all molecules and increase with the number of fluorine atom substituents due to inductive effects. However, the effect of the distant fluorine atoms on the O–H bond strengths is larger than that on the methylene C–H bond strengths, which may be attributed either to the stabilizing effect of oxygen atom acting as a pool of  $\pi$ -electron density to its nearest carbon centered radical or to a greater destabilization of an oxygen-centered than a carbon-centered radical by the inductive effects of fluorine atoms. The latter suggestion is in accordance with the 64.5 kJ mol<sup>-1</sup> difference between the CH<sub>3</sub>O–H and CF<sub>3</sub>O–H bond strengths, versus a much smaller difference of ~27 kJ mol<sup>-1</sup> between the CH<sub>3</sub>CH<sub>2</sub>–H and CF<sub>3</sub>CH<sub>2</sub>–H bond strengths.<sup>13</sup>

**TABLE 9: Comparison of Cl Atom Reactivity with a Series of Fluorinated Ethanols and the Corresponding Fluorinated Ethers and Hydrocarbons (Room-Temperature Rates in  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )**

R/CH <sub>2</sub> OH	<i>k</i> <sub>Cl</sub>	R/OCH <sub>3</sub>	<i>k</i> <sub>Cl</sub>	R/CH <sub>3</sub>	<i>k</i> <sub>Cl</sub>
CH <sub>3</sub> CH <sub>2</sub> OH	95 <sup>a</sup> 90 <sup>b</sup>	CH <sub>3</sub> OCH <sub>3</sub>	191 <sup>c</sup>	CH <sub>3</sub> CH <sub>3</sub>	65.1 <sup>d</sup> 57.5 <sup>e</sup>
CH <sub>2</sub> FCH <sub>2</sub> OH	19.6 ± 2.9 <sup>f</sup>	CH <sub>2</sub> FOCH <sub>3</sub>		CH <sub>2</sub> FCH <sub>3</sub>	6.7 <sup>b</sup> 0.7 <sup>b</sup>
CHF <sub>2</sub> CH <sub>2</sub> OH	2.95 ± 0.39 <sup>f</sup>	CHF <sub>2</sub> OCH <sub>3</sub>		CHF <sub>2</sub> CH <sub>3</sub>	0.27 <sup>b</sup> 0.02 <sup>b</sup>
CF <sub>3</sub> CH <sub>2</sub> OH	0.63 ± 0.09 <sup>f</sup>	CF <sub>3</sub> OCH <sub>3</sub>	0.14 <sup>g</sup>	CF <sub>3</sub> CH <sub>3</sub>	0.00002 <sup>b</sup>

<sup>a</sup> Reference 20. <sup>b</sup> Reference 21. <sup>c</sup> Reference 22. <sup>d</sup> Reference 23. <sup>e</sup> Reference 24. <sup>f</sup> This work. <sup>g</sup> Reference 25.

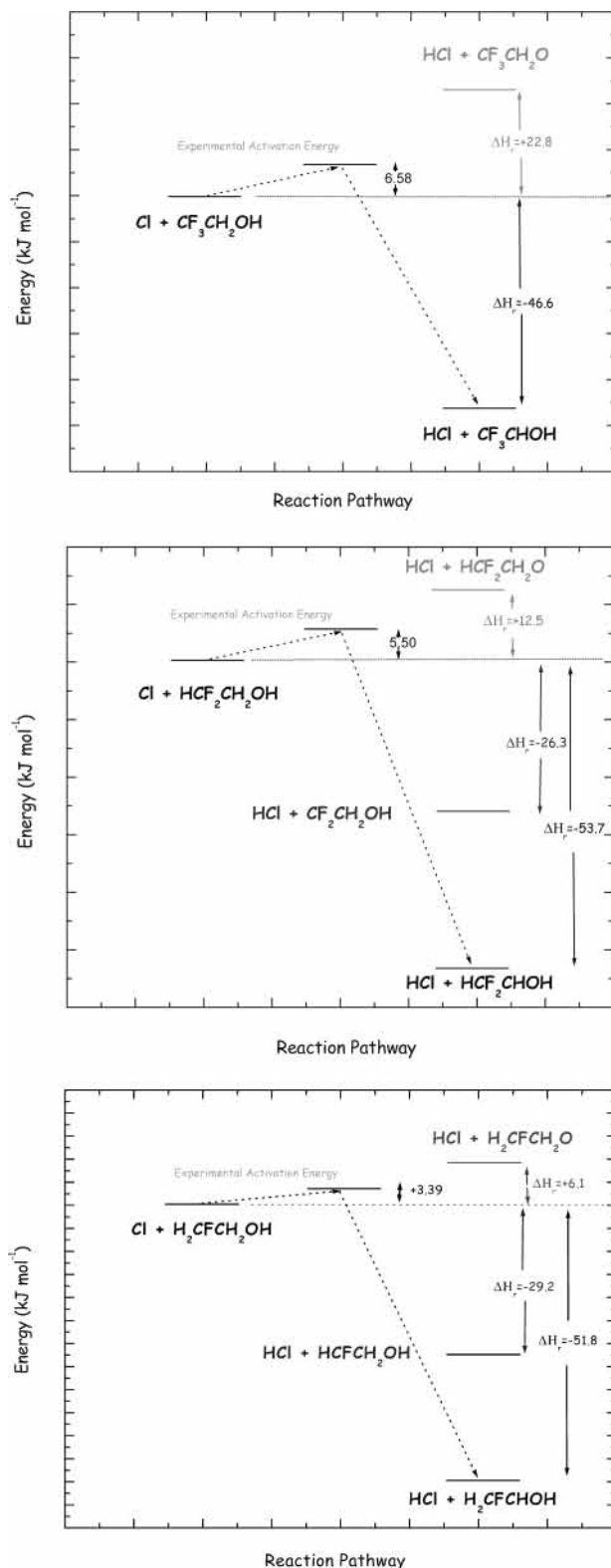
## Discussion and Conclusions

To our knowledge, there are no rate constant data available for the reactions of the title fluoro alcohols with Cl atoms. There are only two rate constant values for the reaction of CF<sub>3</sub>CH<sub>2</sub>OH with OH radicals,<sup>18,19</sup> which may be compared with our reaction rates. The room-temperature rate constant of Cl atoms with CF<sub>3</sub>CH<sub>2</sub>OH is ~6 times faster than that of OH radicals, which is in agreement with the general behavior of hydrocarbons.<sup>15</sup> In addition, the activation energies for the reactions of CF<sub>3</sub>CH<sub>2</sub>OH with Cl atoms and OH radicals are low, taking the values 6.6 ± 0.6 and 7.4 ± 0.5 kJ mol<sup>-1</sup>,<sup>19</sup> respectively, which is rather expected for highly exothermic reactions.

Furthermore, the reactivity of FAs toward Cl atoms may be compared to the reactivity of the corresponding hydrofluoroethers and hydrofluorocarbons, and their reaction rates at room temperature are presented in Table 9. It appears that the reactivity of FAs is always higher. In particular, the reactivity of CF<sub>3</sub>CH<sub>2</sub>OH is 4.5 times higher than that of CF<sub>3</sub>OCH<sub>3</sub> and 4 orders of magnitude higher than that of CF<sub>3</sub>CH<sub>3</sub>. In general, the -OH group activates the neighboring C-H bonds, since the reaction rates of FAs are always higher than those of the corresponding hydrofluorocarbons.

The structure-reactivity relationship for these reactions is difficult to be determined on the basis of the reaction rates and Arrhenius parameters alone. The reactivity of FAs would depend on several parameters, such as the number and position of H atoms, the strength of the particular C-H bonds, the degree and position of fluorination, and the overall molecular geometry. In addition, the -OH group is expected to play a key role in the reactivity of those compounds. The reactivity of fluorinated ethanols toward Cl atoms appears to decrease by about half an order of magnitude upon fluorination, in the following order: CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>2</sub>FCH<sub>2</sub>OH, CHF<sub>2</sub>CH<sub>2</sub>OH, and CF<sub>3</sub>CH<sub>2</sub>OH.

The potential energy diagrams for the title reactions with all reaction pathways are shown in Figure 4. The activation barriers correspond to our experimental values and refer to the primary pathways. The abstraction of the -OH hydrogen is a sufficiently endothermic pathway in all three reactions, and therefore, it is not expected to occur in our experiments. It is well established that the reaction of Cl atoms with CH<sub>3</sub>CH<sub>2</sub>OH takes place predominantly (~93%) via the abstraction of methylene hydrogen, and to a much lesser extent (~7%) via the methyl hydrogen.<sup>20</sup> Thus, the reaction of CF<sub>3</sub>CH<sub>2</sub>OH is expected to occur mainly via abstraction of -CH<sub>2</sub> hydrogen (reaction 1a), and theoretical calculations appear to support this conclusion. For the reactions of CH<sub>2</sub>FCH<sub>2</sub>OH and CHF<sub>2</sub>CH<sub>2</sub>OH, there are two exothermic reaction pathways, abstraction of either methyl or methylene hydrogen atom. The theoretical calculations show that the C-H bond strengths in CH<sub>2</sub>FCH<sub>2</sub>OH and CHF<sub>2</sub>CH<sub>2</sub>OH are lower in methylene than in methyl groups by ~25 kJ



**Figure 4.** Potential energy diagrams for the title reactions at the B3P86/6-311++G(3df,2p) level of theory. The activation energy corresponds to the experimental value.

mol<sup>-1</sup>, as seen in Table 8. Hence, the predominant reaction pathway in all three reactions is suggested to be the abstraction of methylene hydrogen (reactions 1a, 2a, and 3a), although a minor contribution of the methyl hydrogen abstraction (reactions 2b and 3b) cannot be excluded.

Environmental concerns from the release of FAs in the atmosphere may arise either from their global warming potential

and/or from the possibly negative environmental impact of their degradation products. However, FAs exhibit a higher reactivity toward Cl atoms than CFCs and hydrochlorofluorocarbons (HCFCs), and similar behavior is expected to hold for OH radicals; therefore, FAs are expected to be chemically decomposed in the troposphere in shorter lifetimes. In particular, for the least reactive  $\text{CF}_3\text{CH}_2\text{OH}$  the atmospheric lifetime is estimated to be  $\sim 107$  days, by taking  $k_{\text{OH}} = 10.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (ref 19) and an average global concentration of  $\text{OH} \sim 1 \times 10^6 \text{ molecule cm}^{-3}$ .<sup>26</sup>

The atmospheric degradation of the title FAs will lead primarily to the formation of fluoroacetaldehydes, which are further converted into several intermediate species that result in the probably unstable  $\text{CH}_x\text{F}_{3-x}\text{OOCH}_x\text{F}_{3-x}$ , fluoromethanes,  $\text{CO}_2$ , and HF as final products.<sup>27</sup> In the presence of NO the atmospheric degradation of FAs will also produce  $\text{NO}_2$  and  $\text{CH}_x\text{F}_{3-x}\text{C(O)ONO}_2$ . Ultimately, the tropospheric lifetimes of FAs are expected to be shorter compared to those of earlier CFC substitutes (HCFC, HFC), in terms of chemical reactivity. They may be even a better choice than hydrofluoroethers (HFEs) as CFC alternatives, since they are more hydrophilic and therefore may be removed from the troposphere via precipitation.

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