

Atmospheric Chemistry of CF₃O Radicals: Reaction with H₂O

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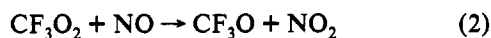
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Evidence is presented that CF₃O radicals react with H₂O in the gas phase at 296 K to give CF₃OH and OH radicals. This reaction is calculated to be exothermic by 1.7 kcal mol⁻¹ implying a surprisingly strong CF₃O–H bond energy of 120 ± 3 kcal mol⁻¹. Results from a relative rate experimental study suggest that the rate constant for the reaction of CF₃O radicals with H₂O lies in the range (0.2–40) × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹. Implications for the atmospheric chemistry of CF₃O radicals are discussed.

Introduction

Recognition of the adverse effect of chlorofluorocarbon (CFC) release into the atmosphere has led to an international effort to replace CFCs with environmentally acceptable alternatives.^{1–3} Hydrofluorocarbons (HFCs) are under consideration as CFC substitutes. For example, HFC-134a is a replacement for CFC-12 in automotive air conditioning systems. Prior to large-scale industrial use, the environmental consequences of release of HFCs into the atmosphere are being considered.⁴ To define the environmental impact of HFC release, the atmospheric photo-oxidation products of HFCs need to be determined.

CF₃ radicals are produced during the oxidation of HFC-134a,^{5,6} HFC-125,^{7–9} and HFC-23.¹⁰ In the atmosphere, CF₃ radicals react with O₂ to give CF₃O₂ radicals which, in turn, react rapidly with NO to form CF₃O radicals:^{11,12}



The atmospheric fate of CF₃O radicals is uncertain and the subject of a significant current research effort. Recently, it has been shown that CF₃O radicals react with NO^{13,14} and organic compounds.^{14–16} To the best of our knowledge, the reaction of CF₃O with H₂O has not been considered as an atmospheric loss mechanism for CF₃O radicals. We report herein results from a computational and experimental study of reaction (3). Our results suggest that reaction (3) may play an important role in the atmospheric chemistry of CF₃O radicals.

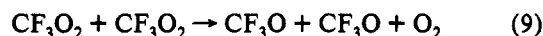
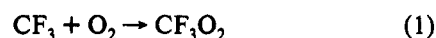
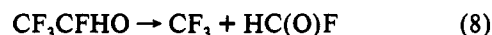
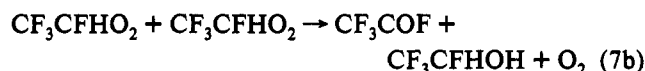
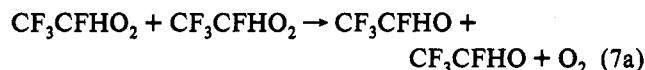
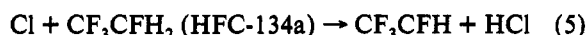
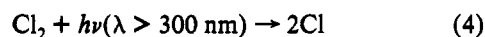


Computational and Experimental Details

Experimental Details. The experimental setup used for the present work has been described previously¹⁷ and is only briefly discussed here. The apparatus consists of a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer interfaced to a 140-L, 2-m long evacuable Pyrex chamber. White type multiple reflection optics were mounted in the reaction chamber to provide a total path length of 26.6 m for the IR analysis beam. The spectrometer was operated at a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32 co-added interferograms.

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CF₃O radicals were generated by the chlorine-initiated oxidation of HFC-134a. Chlorine atoms were generated by the photolysis of molecular chlorine using the output of 22 UV fluorescent lamps (GTE F40BLB). CF₃O radicals are formed by the following reactions:^{6,16}



Initial concentrations were as follows: HFC-134a, 10–1040 mTorr; Cl₂, 296–447 mTorr; and H₂O, 0–916 mTorr. In all experiments, ultrapure air was used as diluent at a total pressure of 700 Torr. The temperature was 296 ± 2 K.

With the exception of CF₃OH, products were quantified by fitting reference spectra of the pure compounds to the observed product spectra using integrated absorption features. Reference spectra were obtained by expanding known volumes of the reference material into the long-path-length cell. Systematic uncertainties associated with quantitative analyses using these reference spectra are estimated to be <10%. CF₃OH was identified by virtue of its characteristic absorption at 3600–3700 cm⁻¹ and quantified using $\sigma_{3664\text{cm}^{-1}}(\text{CF}_3\text{OH}) = 9 \times 10^{-19}$ cm² molecule⁻¹.¹⁶ Systematic uncertainties in the analysis of CF₃OH are estimated to be <15%.

The procedure was as follows. HFC-134a was first quantified and subtracted from the product spectra using characteristic absorption features over the wavelength region 800–1500 cm⁻¹. HC(O)F, CF₃COF, COF₂, CF₃O₂CF₃, and CF₃OH were then identified and quantified using features over the following wavelength ranges: 1700–1900, 1000–1200 and 1800–2000, 700–800 and 1800–2000, 700–900 and 1100–1400, and 3600–3700 cm⁻¹, respectively.

HFC-134a, Cl₂, CF₃COF, and COF₂ were purchased from commercial vendors at purities ≥99%. HC(O)F was prepared

TABLE I: MP2/6-31G*(d,p) Optimized Bond Distances (angstroms) and Bond Angles (degrees). X_{ip} (In-Plane) and X_{op} (Out-of-Plane) Refer to the Two Symmetry-Unique Sets of C-Bound F or H Atoms under C_s Symmetry

	CF ₃ OH	CF ₃ O	CH ₃ OH	CH ₃ O
r(C-O)	1.3493	1.3662	1.4198	1.3850
r(C-X _{ip})	1.3307	1.3364	1.0852	1.0956
r(C-X _{op})	1.3502	1.3367	1.0919	1.0911
r(O-H)	0.9655		0.9622	
∠(O-C-X _{ip})	108.30	105.81	106.52	104.93
∠(O-C-X _{op})	112.19	111.78	112.43	112.54
∠(H-O-C)	108.11		107.32	
∠(X _{ip} -C-X _{op})	108.78	109.87	108.35	107.76
∠(X _{op} -C-X _{op})	106.52	107.75	108.58	110.90

TABLE II: MP4(FC)/6-311+G(d,p)//MP2/6-31G(d,p) Electronic Energies, along with Zero-Point and Internal Energy Corrections to 298.15 K Obtained from the MP2/6-31G(d,p) Geometries and Vibrational Spectra (All Energies in au)

	sym	state	MP4 energy	ZPE	ΔE ^{298.15}	total
CF ₃ OH	C _s	1A'	-412.726 47	0.029 69	0.004 38	-412.731 09
CF ₃ O	C _s	2A'	-412.071 23	0.016 64	0.004 18	-412.050 42
CH ₃ OH	C _s	1A'	-115.477 29	0.053 04	0.003 39	-115.420 86
CH ₃ O	C _s	2A'	-114.803 09	0.038 58	0.002 97	-114.761 55
H ₂ O	C _{2v}	1A ₁	-76.287 03	0.021 90	0.002 83	-76.262 30
HO	C _{∞v}	2Π	-75.595 39	0.008 76	0.002 36	-75.584 28
CH ₄	T _d	1A	-40.405 14	0.046 61	0.020 86	-40.355 67
CH ₃	D _{3h}	2A ₂ '	-39.731 91	0.030 76	0.003 31	-39.697 84
H ₂	D _{∞h}	1Σ _g ⁺	-1.167 69	0.010 50	0.002 36	-1.154 83
H	K _h	2S	-0.499 81	0.0	0.001 42	-0.498 39

from the reaction of benzoyl chloride with dry formic acid and anhydrous potassium fluoride.¹⁸ CF₃O₃CF₃ was prepared by the UV irradiation of CF₃H-F₂-O₂-He mixtures.¹⁹

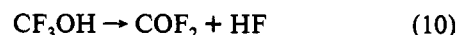
Computational Details. All calculations were performed with the Gaussian 88 program and employed standard basis sets.²⁰ The structures of all molecules were obtained by gradient optimization at the MP2/6-31G(d,p) level (unrestricted MP2 for the radicals). The structures of the first-row hydrides are consistent with MP2/6-31G(d) geometries reported previously, with the addition of a small but uniform decrease in all X-H bond distances arising from the additional hydrogen polarization functions included in our calculations.²¹ Table I contains the optimized parameters for trifluoromethanol,²² trifluoromethoxy radical,²³ methanol,²¹ and methoxy radical.²⁴ Again, all are consistent with earlier results at various lower levels of theory. Using the MP2/6-31G(d,p) geometries, single-point energies were evaluated at the UMP4/6-311+G(d,p) level, keeping the core orbitals frozen in the perturbation calculation. The resultant total energies for all molecules included in this study are reported in Table II.

The force constant matrices and harmonic vibrational frequencies for all molecules were obtained by numerical differentiation of the analytical MP2/6-31G(d,p) gradients. Again, the results parallel those reported earlier for the first-row hydrides.²⁵ The vibrational frequencies were used unscaled to obtain zero point vibrational energies. Internal translational, rotational, and vibrational energy corrections to 298.15 K were calculated using standard statistical mechanical methods.^{26,27} The low-frequency torsions in the two alcohol molecules, along with the umbrella mode of methyl radical, were treated as free rotations and thus contributed RT/2 to the internal energy. While inclusion of zero point energies has a substantial (up to 3 kcal/mol) effect on the calculated reaction heats, the thermal corrections have a fairly minor impact (<0.5 kcal/mol) on our final results.

Experimental Results

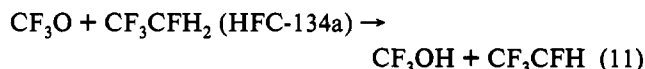
Ten experiments were performed as part of the present work. The experimental conditions and observed product yields are given in Table III. The first experiment involved the UV irradiation

of a mixture of 1.04 Torr of HFC-134a and 300 mTorr of Cl₂, in 700 Torr of air diluent. Figure 1A,B show spectra taken before and after 240 s irradiation of the mixture in experiment no. 1. Comparison with reference spectra of HC(O)F and CF₃OH given in panel 1C clearly shows the formation of these two products. In addition, CF₃COF, COF₂, and CF₃O₃CF₃ were detected. The observed product yields are given in Table III. In experiments with initial HFC-134a concentrations of 1 Torr the IR features attributable to HFC-134a were saturated; consequently the loss of HFC-134a could not be quantified. When the reaction mixture from experiment no. 1 was allowed to stand in the dark the CF₃OH was observed to decay rapidly to give COF₂. The decay is attributed to heterogeneous decomposition on the reactor walls:¹⁶



Within the experimental uncertainties, the decay of CF₃OH followed first-order kinetics with a lifetime of 100 ± 10 s. This loss rate is nearly 200 times faster than we observed in our previous study of CF₃OH.¹⁶ Clearly, the walls of the reaction chamber are now much more reactive toward CF₃OH decomposition. The explanation of the dramatic increase in the wall reactivity probably lies in the recent movement of the experimental system from one building to another. During the move the chamber was exposed to room air for a period of 1 month. In an attempt to recondition the chamber, several experiments were performed in which mixtures of 5–10 Torr of HFC-134a and 1 Torr of Cl₂ were irradiated to expose the chamber walls to high concentrations of CF₃OH. Unfortunately, no conditioning was observed. Throughout the present work the lifetime of CF₃OH remained at 100 ± 10 s.

Experiment no. 2 was essentially a repeat of no. 1 with the addition of 460 mTorr of H₂O. Figure 1D,E show IR spectra before and after 240 s irradiation. For clarity the H₂O features have been removed from 1E. Comparison of panels 1B and 1E shows that the yields of HC(O)F and CF₃OH were unaffected by the presence of H₂O. Similarly, the yields of CF₃COF, COF₂, and CF₃O₃CF₃ were unchanged by the presence of H₂O. In a recent study of the products from the simulated atmospheric oxidation of HFC-134a we have shown that CF₃OH is produced from the reaction of CF₃O radicals with HFC-134a, and that this reaction has a rate constant of $k_{11} = (1.1 \pm 0.7) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁶ Reaction 11 competes with reaction 12 for the



available CF₃O radicals. From experiment nos. 1 and nos. 2 it is clear that the addition of 460 mTorr of H₂O to a reaction mixture containing approximately 1 Torr of HFC-134a causes no observable change (<10%) of CF₃OH formation when the mixtures are irradiated. Hence, 460 mTorr of H₂O is less than 10% as effective as 1030 mTorr of HFC-134a. As $k_{11} < 1.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, then $k_3 < 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Further investigation of the kinetics of reaction 3 requires use of larger values of the [H₂O]/[HFC-134a] concentration ratio. The presence of moisture-sensitive optical components in the reaction chamber makes the use of significantly increased [H₂O] undesirable. Therefore, the ratio [H₂O]/[HFC-134a] was increased by decreasing [HFC-134a]. Experiment nos. 3–10 were conducted using [HFC-134a]₀ = 9.9–24.1 mTorr. With such low initial concentrations the expected yields of CF₃OH are close to, or below, the detection limit of approximately 1 mTorr, which precludes direct measurement of the CF₃OH yield. Instead, the formation of CF₃OH was measured indirectly by observing the yield of COF₂ formed after reaction mixtures were left to stand

TABLE III: Product Yields^a following the Irradiation of HFC-134a/Cl₂/H₂O Mixtures in 700 Torr of Air

expt	[HFC-134a] ₀	[Cl ₂] ₀	[H ₂ O] ₀	t _{UV} (s)	[Δ[HFC-134a]]	Δ[HC(O)F]	Δ[CF ₃ COF]	Δ[CF ₃ O ₂ CF ₃]	Δ[COF ₂]	Δ[CF ₃ OH]
1	1040	296	0	75 ^b	na ^c	11.1	3.3	3.9	1.0	2.4
				240 ^b	na	35.7	10.2	9.7	9.6	4.3
2	1030	296	460	75 ^b	na	10.6	3.0	2.4	0.9	2.1
				240 ^b	na	35.7	10.2	10.2	9.7	4.0
3	9.9	438	0	180 ^c	2.28	1.38	0.51	0.58	0.47	
4	10.1	444	502	180 ^c	2.42	1.39	0.49	0.53	0.57	
						(57%) ^d	(20%)	(22%)	(24%)	
5	10.1	444	786	180 ^c	2.32	1.35	0.51	0.50	0.67	
						(58%)	(22%)	(22%)	(29%)	
6	10.1	444	916	180 ^c	2.12	1.46	0.45	0.39	0.68	
						(69%)	(21%)	(18%)	(32%)	
7	23.8	444	0	180 ^c	4.76	2.83	0.96	1.21	0.85	
						(59%)	(20%)	(25%)	(18%)	
8	23.8	444	358	180 ^c	4.52	2.77	0.95	0.81	0.90	
						(61%)	(21%)	(18%)	(20%)	
9	24.1	447	0	300 ^c	7.23	3.94	1.56	1.69	1.24	
						(55%)	(22%)	(23%)	(17%)	
10	24.1	447	706	300 ^c	7.23	3.94	1.50	1.59	1.46	
						(55%)	(21%)	(22%)	(20%)	

^a Observed concentrations in units of mTorr, with no corrections of any kind applied to data. ^b Irradiation time, analysis performed immediately after irradiation. ^c Irradiation time, analysis performed after reaction mixture sat in dark for 10 min to allow complete decomposition of CF₃OH into COF₂. ^d Values in parentheses are molar yields relative to HFC-134a loss. ^e Not available.

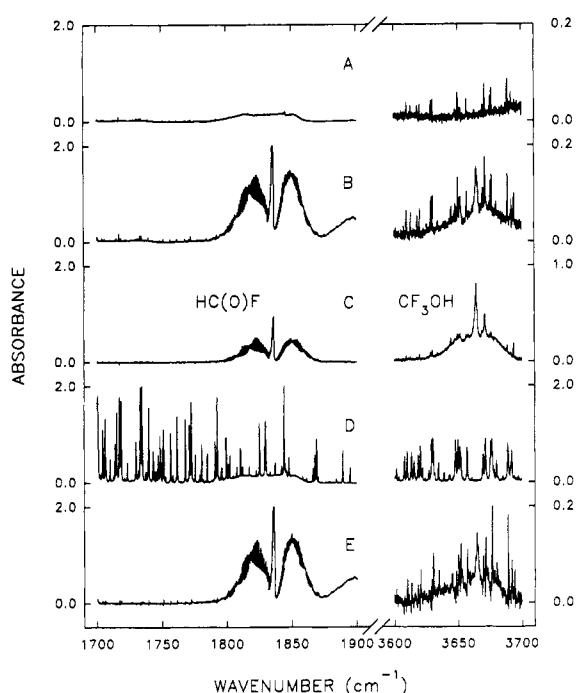


Figure 1. Spectra taken before (A) and after (B) 240-s irradiation of a mixture of 1.04 Torr of HFC-134a and 296 mTorr of Cl₂, in 700 Torr of air diluent. Comparison with reference spectra of HC(O)F and CF₃OH given in panel 1C shows the formation of these products. Spectra D and E were acquired before and after 240-s irradiation of a mixture of 1.03 Torr of HFC-134a, 296 mTorr of Cl₂, and 460 mTorr of H₂O. The H₂O features in panel E have been subtracted for clarity.

for 10 min in the dark. As discussed above, CF₃OH rapidly decomposes into COF₂ in the reaction chamber. The detection limit of COF₂ was 0.02 mTorr. Reported product yields in Table III for experiment nos. 3–10 were measured after all dark chemistry had ceased (after 10 min). In all cases, within the experimental uncertainties, the yields of HC(O)F and CF₃COF were unaffected by the presence of H₂O. In contrast, the yield of COF₂ increased significantly with increased [H₂O]. Conversely, the measured CF₃O₂CF₃ yield decreased with increased [H₂O]. This observation is consistent with a competition between reactions 3 and 12 for the available CF₃O radicals.

To illustrate these observations, Figure 2A,B shows spectra acquired before and after irradiation of a mixture of 9.9 mTorr of HFC-134a and 438 mTorr of Cl₂ in 700 Torr of air (experiment

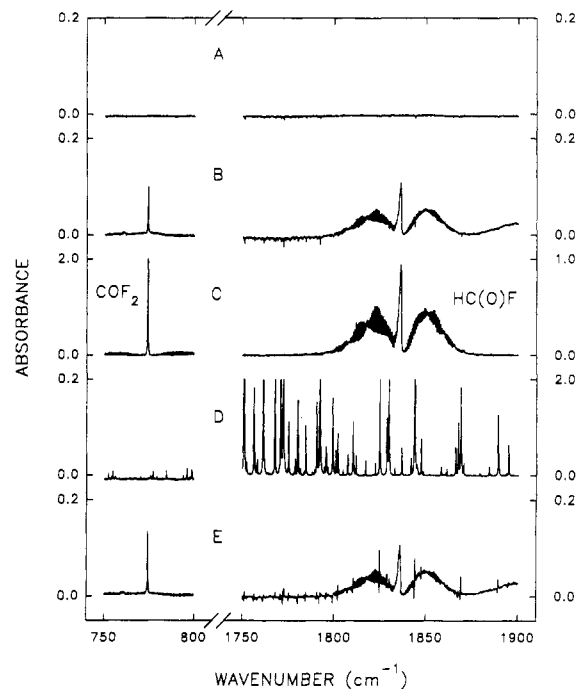


Figure 2. Spectra taken before (A) and after (B) 180-s irradiation of a mixture of 9.9 mTorr of HFC-134a and 438 mTorr of Cl₂, in 700 Torr of air diluent. Comparison with reference spectra of HC(O)F and COF₂ given in panel 1C shows the formation of these products. Spectra D and E were acquired before and after 180-s irradiation of a mixture of 10.1 mTorr of HFC-134a, 444 mTorr of Cl₂, and 916 mTorr of H₂O. The H₂O features in panel E have been subtracted for clarity.

no. 3). Figure 2D,E shows spectra taken before and after irradiation of the reaction mixture used in experiment no. 6. Experiment no. 6 was essentially a repeat of no. 3 but with 916 mTorr of H₂O added. For clarity H₂O features in 2E have been subtracted. Comparison of Figures 2B,E with reference spectra of COF₂ and HC(O)F (given in panel 2C) shows that these species are products and that the yield of COF₂ is significantly larger in the presence of H₂O.

The ratio of the COF₂ yield in the presence of H₂O to that observed in the absence of H₂O is plotted as a function of the concentration ratio [H₂O]/[HFC-134a] in Figure 3. The solid line is a linear least squares fit forced through a y-axis intercept of unity. Assuming that (i) COF₂ is formed solely from the decomposition of CF₃OH, (ii) reactions 3 and 11 are the only

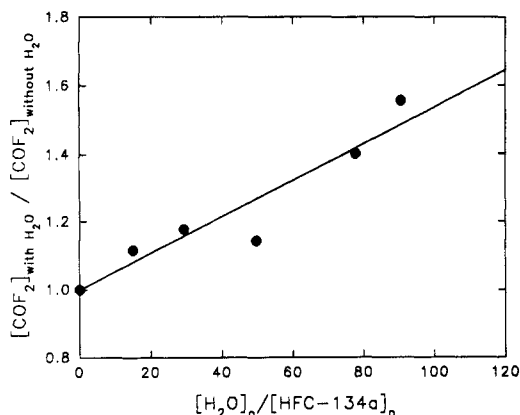


Figure 3. Ratio of COF₂ yield observed in the presence of H₂O to that observed in the absence of H₂O versus [H₂O]₀/[HFC-134a]₀; see text for details.

TABLE IV: Reaction Mechanism

reaction	$k(296 \pm 2 \text{ K})^a$
Cl ₂ → 2Cl	
Cl + CF ₃ CFH ₂ → HCl + CF ₃ CFH	1.4×10^{-15}
CF ₃ CFH + O ₂ → CF ₃ CFHO ₂	2×10^{-12}
CF ₃ CFHO ₂ + CF ₃ CFHO ₂ → 2CF ₃ CFHO + O ₂	6×10^{-12}
CF ₃ CFHO ₂ + CF ₃ CFHO ₂ → CF ₃ COF + CF ₃ CFHOH + O ₂	1×10^{-12}
CF ₃ CFHO ₂ + CF ₃ O ₂ → CF ₃ CFHO + CF ₃ O + O ₂	8×10^{-12}
CF ₃ CFHO → CF ₃ + HC(O)F	2×10^4
CF ₃ CFHO + O ₂ → CF ₃ COF + HO ₂	9×10^{-16}
CF ₃ + O ₂ → CF ₃ O ₂	8.5×10^{-12}
CF ₃ O ₂ + CF ₃ O ₂ → CF ₃ O + CF ₃ O + O ₂	1.8×10^{-12}
CF ₃ O + CF ₃ O ₂ → CF ₃ O ₃ CF ₃	2.5×10^{-11}
CF ₃ O + CF ₃ CFHO ₂ → CF ₃ CFHO ₃ CF ₃	1.8×10^{-11}
CF ₃ CFHO ₃ CF ₃ → CF ₃ CFHO ₂ + CF ₃ O	$5.0 \times 10^{-3} \text{ }^{b,c}$
→ CF ₃ CFHO + CF ₃ O ₂	$5.0 \times 10^{-3} \text{ }^{b,c}$
CF ₃ O + CF ₃ CFH ₂ → CF ₃ CFH + CF ₃ OH	4.5×10^{-16}
CF ₃ OH → CF ₂ O + HF	$1 \times 10^{-2} \text{ }^{b,d}$
Cl + HC(O)F → HCl + FCO	2.0×10^{-15}

^a Units of cm³ molecule⁻¹ s⁻¹. ^b Units of s⁻¹. ^c Assumed equal to rate of CF₃OH decomposition. ^d Measured in this work.

sources of CF₃OH, and (iii) formation of CF₃OH is a relatively minor fate of CF₃O radicals (i.e., there are CF₃O radicals available which can be diverted by reaction with H₂O to give CF₃OH), then the following expression holds:

$$Y(\text{COF}_2)_{\text{H}_2\text{O}}/Y(\text{COF}_2) = 1 + (k_3/k_{11})([\text{H}_2\text{O}]/[\text{HFC-134a}])$$

$Y(\text{COF}_2)_{\text{H}_2\text{O}}$ is the molar yield of COF₂ observed when H₂O is present, $Y(\text{COF}_2)$ is the corresponding yield when H₂O is absent, and k_3/k_{11} is the ratio of the rate constants for reactions 3 and 11. Linear least-squares analysis of the data in Figure 3 gives $k_3/k_{11} = (5.4 \pm 1.3) \times 10^{-3}$. The quoted error represents 2 standard deviations.

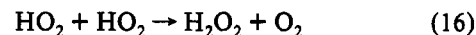
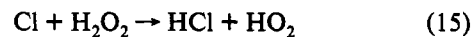
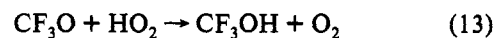
Discussion of Experimental Results

The observed product yields given in Table III can be compared to those expected based upon recent studies of the Cl atom initiated oxidation of HFC-134a in our laboratory.¹⁶ The Acuchem chemical kinetic modeling program²⁸ together with the mechanism in Table IV (taken from ref 16) was used to calculate the expected product yields. In experiment no. 1 we could not quantify the loss of HFC-134a, so absolute yields for the HC(O)F, CF₃COF, CF₃O₃CF₃, COF₂, and CF₃OH are unknown. However, we can compare the observed yields on a relative basis. Relative to HC(O)F, the yields of CF₃COF, CF₃O₃CF₃, COF₂, and CF₃OH after 240 s of irradiation were 29%, 27%, 27%, and 12% respectively. Simulation of experiment no. 1 using the chemical mechanism given in Table IV predicts yields of 28%, 31%, 20%,

and 13% for these species, reasonably consistent with the experimental observations. The results from experiment nos. 1 and 2 were indistinguishable, and hence the latter can also be adequately simulated using the mechanism in Table IV.

In contrast, for nos. 3, 7, and 9 the mechanism in Table IV grossly underpredicts the COF₂ yield. For example, under the experimental conditions of no. 3 the predicted HC(O)F, CF₃COF, CF₃O₃CF₃, and COF₂ yields are 70%, 20%, 31%, and 1% compared to the observed yields of 61%, 22%, 25%, and 21%, respectively. The mechanism in Table IV has only one process that forms CF₃OH and hence COF₂—namely reaction of CF₃O with HFC-134a. Clearly, for the experimental conditions of experiment no. 3, additional reactions that form either CF₃OH, or COF₂, or both, are missing from the mechanism in Table IV. As discussed previously,¹⁶ in addition to HFC-134a, other hydrogen-containing species are present with which CF₃O radicals can react. Examples include, HC(O)F, HO₂ radicals (formed from the reaction of CF₃CFHO radicals with O₂), H₂O₂ (formed by the self-reaction of HO₂ radicals), CF₃OOH (formed by the reaction of CF₃O₂ with HO₂), and CF₃CFHOH (a product of reaction 7b). These, and other, possibilities were considered and shown to be of minor importance in our previous investigation of the source of CF₃OH following irradiation of HFC-134a/Cl₂/air mixtures with initial concentrations of HFC-134a of approximately 1 Torr. However, such reactions may be important in experiments employing lower HFC-134a concentrations.

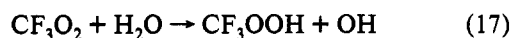
To provide insight into the possible impact of reactions of CF₃O with hydrogen containing species other than HFC-134a, reactions 13–16 were added to the chemical mechanism with $k_{13} = 1.1 \times$



10^{-10} , $k_{14} = 1.7 \times 10^{-12}$, $k_{15} = 4.1 \times 10^{-13}$, and $k_{16} = 3.0 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Kinetic data were taken from ref 29. As noted previously,¹⁶ the reactivity of CF₃O radicals towards hydrocarbons is comparable to that of OH radicals. Reactions 13 and 14 were assumed to proceed at the same rate as the corresponding OH radical reactions. For experiment no. 3, the inclusion of reactions 13–16 does not change the predicted yields for HC(O)F and CF₃COF. However, the yields of CF₃O₃CF₃ and COF₂ change to 25% and 17%, respectively. These yields are consistent with those experimentally observed. Inclusion of reactions 13–16 in a simulation of experiment no. 1 gives predicted yields of CF₃COF, CF₃O₃CF₃, COF₂, and CF₃OH relative to HC(O)F (28%, 24%, 29%, and 18%, respectively) that are close to those experimentally observed. The agreement between the predicted yields based upon the mechanism which includes reactions 13–16 suggests but does not prove that these reactions are important. Uncertainties remain in our understanding of the mechanism(s) by which COF₂ is formed in experiments employing low HFC-134a concentrations.

The purpose of the present work is to search for evidence for reaction 3, not to study the reaction mechanism of the Cl atom initiated oxidation of HFC-134a. Modeling of the product yields was not pursued further. While imperfect, the chemical mechanism given in Table IV, with reactions 13–16 added, provides insight into the complex chemistry occurring. As seen from Table III, the addition of H₂O to reaction mixtures containing low initial HFC-134a concentrations leads to an increase in the yield of COF₂ and a decrease in that of CF₃O₃CF₃. In contrast, the observed yields of HC(O)F and CF₃COF were unchanged. The presence of H₂O perturbs the chemistry associated with CF₃O

and/or CF₃O₂ radicals. Two possibilities exist:



with the products, CF₃OH or CF₃OOH, decomposing to give COF₂.

To check on the behavior of CF₃OOH in the chamber an experiment was performed using the UV irradiation of a mixture of 315 mTorr of Cl₂, 17 mTorr of CF₃I, and 4.5 Torr of H₂ in 700 Torr air. Following irradiation, CF₃OOH was identified as a major product by virtue of its characteristic IR absorptions at 1246, 1382, and 3572 cm⁻¹.^{30,31} On standing in the dark for 10 min there was no observable decay of CF₃OOH (<5%). There was also no observable decay when CF₃OOH was left to stand in the dark for 5 min with 275 mTorr of H₂O added to the reaction mixture. We conclude that reaction 17 does not contribute to the increased COF₂ yield observed in experiment nos. 3–10 when H₂O is added.

The possible reaction of CF₃O and CF₃O₂ radicals with species on the reaction chamber walls needs consideration. Using the mechanism consisting of Table IV plus reactions 13–16 the lifetimes of CF₃O and CF₃O₂ radicals in the chamber with respect to gas phase reactions are calculated to be <100 and <600 ms respectively. These lifetimes preclude significant interaction with the chamber walls.

Finally, we need to consider the possibility that the trioxide, CF₃O₃CHF₂, which is a short-lived product observed during the simulated atmospheric oxidation of HFC-134a,¹⁶ may react with H₂O to form either CF₃OH or COF₂. CF₃O₃CHF₂ decomposes into either CF₃O₂ and CF₃CHFO, or CF₃O and CF₃CFHO₂ radicals.¹⁶ Reaction with H₂O may compete with decomposition. However, such a competition would not be affected by the HFC-134a concentration used. Hence, if reaction of CF₃O₃CHF₂ with H₂O was important then increased CF₃OH and/or COF₂ yields would be expected in experiments using both high and low initial HFC-134a concentrations. This is inconsistent with the experimental observations (for example, compare experiment nos. 2 and 4 in Table III) suggesting that reaction of CF₃O₃CHF₂ with H₂O is not a complication in the present work.

We believe that the most likely explanation for the observed increase of COF₂ product on addition of H₂O is the gas-phase reaction of CF₃O radicals with H₂O. To derive a value for *k*₃, we need to construct a chemical mechanism which accurately predicts the product yields observed in the absence of H₂O. Then we need to add reaction 3 to the model and optimize *k*₃ to reproduce the experimentally observed product yields in the presence of H₂O. Unfortunately, as discussed above, the mechanism by which COF₂ is formed in experiments using low HFC-134a concentrations is not completely understood. Thus, it is difficult to estimate the rate constant *k*₃. However, we note that because of the presence of sources of CF₃OH, and thereby COF₂ other than reaction 11, the rate constant ratio *k*₃/*k*₁₁ derived from the data in Figure 3 is a lower limit. Hence, *k*₃/*k*₁₁ > (5.4 ± 1.3) × 10⁻³, using *k*₁₁ = (1.1 ± 0.7) × 10⁻¹⁵ then gives *k*₃ > 2 × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹.

Computational Results and Discussion

That reaction 3 should proceed spontaneously in the gas phase is interesting for two reasons: first, the reaction has important implications for the atmospheric chemistry of CF₃O radicals; second, it implies a remarkably strong O–H bond in CF₃O–H, far stronger than that observed for any other alcohol. The O–H bond in water is among the strongest single bonds known (119.2 kcal/mol).³² By comparison, the O–H bond dissociation energy in methanol, which is typical of most all alcohols, is 104.4 kcal/mol.^{33a} For reaction 3 to occur spontaneously, as the experimental

TABLE V: Computationally Determined Heats of Hydrogen Exchange along with Available Experimental Heats of Reaction, from Bond Energy Measurements (All Energies in kcal/mol)

	$\Delta H_{\text{calc}}^{298}$	$\Delta H_{\text{exp}}^{298}$
CF ₃ O + H ₂ O → CF ₃ OH + OH	-1.7	
CF ₃ O + CH ₄ → CF ₃ OH + CH ₃	-14.3	
CF ₃ O + H ₂ → CF ₃ OH + H	-15.2	
CH ₃ O + H ₂ O → CH ₃ OH + OH	11.7	14.6
CH ₃ O + CH ₄ → CH ₃ OH + CH ₃	-0.9	0.4
CH ₃ O + H ₂ → CH ₃ OH + H	-1.8	-0.2

results suggest, the O–H bond in trifluoromethanol must be comparable in strength to that in water, or 15 kcal/mol stronger than for a typical alcohol. Such a result is quite surprising. The anomalous behavior of trifluoromethyl compounds has been noted previously, both in the unusually large O–O bond strength in bis(trifluoromethyl) peroxide³⁴ and the unusual stability of the bis(trifluoromethyl) trioxide. Trifluoromethanol appears to present yet another example of this curious behavior.

Clearly, an accurate value for the CF₃O–H bond strength is needed, both to establish the thermodynamic feasibility of reaction 3 and to compare with water and other alcohols. Unfortunately, its direct evaluation either experimentally or computationally is quite difficult. In particular, direct calculation of bond scission energies is notoriously inaccurate because of the overriding importance of correlation in describing the electron pairing process.²⁵ However, computational methods can be used to evaluate to a reasonable level of accuracy the energies of reactions in which the total number of unpaired electrons is conserved (isogyric reactions), and in particular to obtain useful energetic trends among reactions of a similar type. To this end, we have calculated the heat of reaction of CF₃O with water, methane, and hydrogen. Additionally, the heats of the corresponding CH₃O reactions were calculated for comparison with the available experimental results.

Table II contains the raw energy data for all the molecules studied. The energies were obtained by single point calculations at the MP4/6-311+G(d,p) level using fully optimized MP2/6-31G(d,p) geometries. This basis set and degree of correlation were chosen as a compromise between the desired level of accuracy and computational expense, based on our own work and earlier calculations comparing various levels of correlation and extended triple-split-valence bases.³⁵ Even these relatively extensive (and expensive) calculations are not sufficient to obtain accurate absolute molecular energies, but we expect them to provide reasonably accurate (±3 kcal/mol) energy differences for the isogyric reactions. The MP2 vibrational frequencies were used to obtain zero point and thermal corrections to 298.15 K, and Table II also includes these values.

Table V contains the calculated heats of reaction of the methoxy radical with three hydrogen donors, obtained from the thermally corrected total energies in Table II. The table also contains experimental values for the three methoxy reactions, calculated from the X–H bond dissociation energies using the following equation:³³

$$\Delta H^{298.15} = D_{298.15}^{\circ}(\text{CH}_3\text{O}-\text{H}) - D_{298.15}^{\circ}(\text{X}-\text{H})$$

A comparison of the experimental and theoretical results should help establish the accuracy of the computational method. The experimental bond energies are reportedly accurate to ±1 kcal/mol. Thus, we can expect the experimental results in Table V to be accurate to within ±2 kcal/mol. Given this level of uncertainty, the agreement between experimental and computed results is very good. As expected from the experimental data, the reaction of methoxy radical with water is a strongly endothermic process. In contrast, the reactions of methoxy radical with methane and hydrogen are nearly thermoneutral processes, reflecting the similarity of the CH₃O–H, H–H, and CH₃–H bond

strengths. The computational results systematically underestimate the experimental results by 1–3 kcal/mol, or slightly greater than the experimental uncertainty, which probably results from inadequacies in our basis set. However, the computational results have adequate accuracy to address the thermodynamics of reaction 3.

Table V also contains the calculated heats of reaction of the CF₃O radical with the three hydrogen donors. The energies are shifted downward 13.4 kcal/mol relative to the methoxy results. This shift reflects a corresponding increase in the computed O–H bond strength from methanol to trifluoromethanol. In contrast to the CH₃O results, the CF₃O reactions with the hydrogen molecule and methane are predicted to be strongly exothermic processes. Consistent with these results, we have previously observed the reaction of CF₃O radicals with methane in our chamber.¹⁶

The 13.4 kcal/mol shift from the methoxy to trifluoromethoxy case is just enough to make the reaction with water exothermic. We calculate the heat of this reaction to –1.7 kcal/mol. Lower levels of theory, including the MP2/6-31G(d,p) calculations and the MP2 and MP3/6-311+G(d,p) results, give slightly (0–2 kcal/mol) more negative values. Given the likely level of error, and in particular the systematic error observed in the methoxy results, we cannot definitely conclude from the calculations that the reaction is exothermic or spontaneous. However, we can say with confidence that the reaction is close to thermoneutrality and that unlike the reaction of typical alkoxy radicals with water, the abstraction of a hydrogen atom from water by trifluoromethoxy radical is energetically feasible.

While our calculations by themselves do not provide a good estimate of the O–H bond energy in trifluoromethanol, we can combine the heats of reaction in Table V with the experimental bond energies of hydrogen, methane, or water, to obtain an “experimentally corrected” value. Using this approach yields an O–H bond energy of 119–121 kcal/mol, depending on the reaction used. A safe estimate, based on our results, is 120 ± 3 kcal/mol. As already noted, this value is comparable to or greater than the bond energy of water and is roughly 15 kcal/mol greater than that typically observed for an alcohol. Thus, the bond is among the strongest single bonds known.

Implications for Atmospheric Chemistry

In the present work we present computational results which show that the reaction of CF₃O radicals with H₂O is thermodynamically feasible, and experimental results which suggest this reaction has a rate constant that lies in the range $4 \times 10^{-16} > k_3 > 2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K.

At present, the atmospheric loss mechanism for CF₃O radicals is believed to be reaction with NO and hydrocarbons. Bevilacqua et al.¹⁴ and Zellner³⁶ both report rate constants of approximately $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction with NO, while Saathoff and Zellner³⁷ have measured $k(\text{CF}_3\text{O} + \text{CH}_4) = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reasonable estimates for the global tropospheric concentrations of NO, CH₄, and H₂O are 2.5×10^8 (10 ppt), 5×10^{13} (2 ppm), and $3 \times 10^{17} \text{ cm}^{-3}$ (50% relative humidity). Using $k_3 = (0.2\text{--}40) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ then leads to atmospheric lifetimes of CF₃O radicals (at room temperature) with respect to reaction with NO, CH₄, and H₂O of 200, 0.9, and 0.01–1.7 s, respectively. It appears that reaction 3 may play a significant role in the atmospheric chemistry of CF₃O radicals, and hence, in the atmospheric degradation of CFC replacements such as HFC-134a. Further study is required to define k_3 more precisely and to provide kinetic data for the reactions of CF₃O radicals with organic species and H₂O as a function of temperature.

Note Added in Proof. It has recently come to our attention that Dixon at the du Pont Chemical Co. has calculated a CF₃O–H bond strength of 118.5 kcal mol⁻¹. The result obtained by Dixon is in good agreement with our calculations.

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