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Vapor Pressure and Intramolecular Hydrogen Bonding in Fluorotelomer Alcohols

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Vapor pressure and aqueous solubility are important parameters used to estimate the potential for transport of chemical substances in the atmosphere. For fluorotelomer alcohols (FTOHs), currently under scrutiny by environmental scientists as potential precursors of persistent perfluorocarboxylates (PFCAs), vapor pressure is the more significant property since these compounds are only very sparingly soluble in water. We have measured the vapor pressures of a homologous series of fluorotelomer alcohols, $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2-5$), in the temperature range 21−250 °C by three independent methods: (a) a method suitable for very low vapor pressures at ambient temperatures (gas-saturation method), (b) an improved boiling point method at controlled pressures (Scott method), and (c) a novel method, requiring milligram quantities of substance, based on gas-phase NMR, a technique largely unfamiliar to chemists and holding promise for studies of relevance to environmental chemistry. The concordant values obtained indicate that recently published vapor pressure data overestimate the vapor pressure at ambient temperature, and therefore the volatility, of this series of fluorinated compounds. It was suggested that substantial intramolecular $-O-H\cdots F-$ hydrogen bonding between the hydroxylic proton and the two fluorines next to the ethanol moiety was responsible for their putative high volatility. Therefore, we have used gas-phase NMR, gas-phase FTIR, 2D NMR heteronuclear Overhauser effect measurements, and high-level ab initio computations to investigate the intramolecular hydrogen bonding in fluorotelomer alcohols. Our studies unequivocally show that hydrogen bonding of this type is not significant and cannot contribute to and cause unusual volatility. The substantially lower vapor pressure at ambient temperatures than previously reported resulting from our work is important in developing a valid understanding of the environmental transport behavior of this class of compounds.

Introduction

Perfluorinated compounds such as perfluorosulfonates (e.g., perfluorooctane sulfonate, PFOS) and perfluorocarboxylates (e.g., salts of perfluorooctanoic acid, PFOA, and the acid itself) have gained attention recently since they have been found in trace amounts in human sera in North America and Europe.[1−4] Other studies have reported that PFOS, and to a lesser extent PFOA, are found in wildlife and in the environment.[5−7] In addition to substantial direct-release sources of perfluorocarboxylates in the environment,[8−11] questions have been raised as to whether and to what extent fluorotelomer alcohols (FTOHs) may represent an indirect source of PFOA and other perfluorocarboxylates in the environment.

Fluorotelomer alcohols, $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2-6$), are linear molecules of 6−14 carbons, comprised of a perfluoroalkyl segment of an even number of carbons attached to an ethanol moiety. The nomenclature *n*-2 FTOH specifies the number of fluorinated and hydrogenated carbons in the molecule (e.g., 8-2 FTOH is $CF_3-(CF_2)_7-CH_2-CH_2-OH$). Alternatively, fluorinated alcohols are also termed telomer B alcohols (e.g., 8-2 TBA). They are intermediates in the production of a variety of surface-active fluorotelomer-based polymeric and surfactant products where the low surface energy of the perfluoroalkyl chain produces useful surface properties including water and oil repellency.[12,13]

These compounds, and especially 8-2 FTOH, have been the subject of several recent studies to understand their potential contribution via degradation chemistry to trace amounts of perfluorocarboxylates (PFCAs), including PFOA, detected in the environment. Studies concerned with the occurrence of some fluorotelomer alcohols in the North American troposphere,[7,14] with their atmospheric chemistry[15−17] as well as with their microbial biodegradation,[18,19] have been reported. An earlier study, as well as very recent work, describes the mammalian metabolism of 8-2 FTOH in rats.[20,21] As the environmental and toxicological significance of fluorotelomer alcohols is being investigated and informed by new studies, there is a critical need for reliable analytical methodologies to assay these compounds and their degradation products in biological and environmental matrixes.[22] Similarly, it is critically important to know accurately their physicochemical properties and to understand the effects of their chemical structure on their physical, chemical, and transport behavior.

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For a molecule to be widely present in the environment, long-range transport via water or air is usually required, unless direct local sources are identified. In the case of fluorotelomer alcohols, solubility in water is minimal,[23] and volatility, that is, the vapor pressure at ambient temperatures, becomes the critical property for atmospheric transport. Within this context, the vapor pressures at 25 °C of the fluorotelomer alcohols n-2 FTOH (n = 4, 6, 8, 10) were the subject of two very recent studies.[24,25] In the first study, the vapor pressures at 25 °C were estimated by extrapolating to room temperature measurements obtained by a conventional boiling point method at substantially higher temperatures using the Clausius−Clapeyron equation.[24] These extrapolated ambient temperature values were then used as yardsticks to judge the reliability of environmental models used to predict vapor pressures. The observation that the four models used consistently yielded lower vapor pressures at ambient temperature than the extrapolated values was taken as an indication that the models did not account for a putatively significant −O−H···F− intramolecular hydrogen bonding between the hydroxyl (−OH) hydrogen atom and the two fluorines next to the ethanol moiety. Such hydrogen bonding, inferred from fragmentation patterns in mass spectrometric studies[26] and ^{17}O NMR data,[27] was proposed to impart to fluorotelomer alcohols higher than expected volatility by "masking" the −OH functional group from other molecules. In the second study, the vapor pressures were estimated as a function of temperature using a technique based on measuring gas-chromatographic retention times relative to those of hexachlorobenzene.[25]

In this paper, we report vapor pressure determinations for the same series of fluorotelomer alcohols in the temperature range from 21 to 250 °C by three methods: (a) a method suitable for very low vapor pressures at ambient temperatures (gas-saturation method, FTOH 6-2, 8-2, and 10-2), (b) an improved boiling-point method at controlled pressures (Scott method, FTOH 6-2 and 8-2), and (c) a novel method, requiring milligram quantities of substance, based on gas-phase NMR, a technique largely unfamiliar to chemists and holding promise for studies of relevance to environmental chemistry (FTOH 4-2, 6-2, 8-2, and 10-2). The liquid-phase vapor pressures were extrapolated to ambient temperatures using the Antoine equation. The concordant values obtained for the vapor pressures of these fluorotelomer alcohols at ambient temperatures indicate that in the above-mentioned studies the ambient temperature volatility of this series of compounds was overestimated, in one case by as much as 40−50 times (n = 4). Furthermore, we also show that the −O−H···F− intramolecular hydrogen bonding, postulated to be the cause of the putatively exceptional volatility of these compounds, is not significant as demonstrated by gas-phase NMR, gas-phase FTIR, and 2D NMR Overhauser effect measurements in solution. High-level ab initio computational chemistry for the 2-2 and 4-2 fluorotelomer alcohols do predict a very weak intramolecular hydrogen bonding interaction of about 1 kcal/mol, in agreement with several related molecular systems reported in the literature (e.g., refs 41 and 42). Such weak hydrogen bonding cannot have material consequences on vapor pressure at ambient and higher temperatures. A preliminary report limited to the vapor pressure of the 8-2 fluorotelomer alcohol (8-2 FTOH) was published elsewhere.[23]

Experimental Section

Materials. Fluorotelomer Alcohols. 4-2 FTOH was obtained from Sigma-Aldrich Inc. (97%). 6-2 FTOH was obtained by distillation of a mixture of fluorotelomer alcohols (>96%). 8-2 FTOH (CAS number 678-39-7) was obtained from Clariant, GmbH (Germany) and was shown to be 99.2% pure via gas chromatography (mp 48−50 °C, Clariant). The major impurity (0.8% by area) was tentatively identified as $C_7F_{15}CF{=}CHCH_2$-OH on the basis of the mass spectral fragmentation pattern. 10-2 FTOH was obtained from Lancaster Synthesis (97%, mp 94 °C). The fluorotelomer alcohols were kept and manipulated in a nitrogen glovebox (Vacuum Atmospheres Inc.). Cyclopropane was purchased from Matheson Tri-Gas Company (>99%).

Vapor Pressure by Conventional Techniques. Two conventional techniques were used to determine vapor pressure. The first method is based on a dynamic measurement procedure developed by Scott (the Scott method) wherein the equilibrium temperature is measured at a controlled pressure.[28] It was used to determine the vapor pressures of the 6-2 and 8-2 fluorotelomer alcohols. Approximately 30 g of the fluorotelomer alcohol was placed in a round-bottom flask boiler. The pressure was held constant to 0.01% (0.01 kPa) and was measured to an accuracy of 0.01%. The apparatus consisted of a Mensor PCS400 pressure controller (San Marcos, TX), a Paroscientific 740 pressure transducer (Redmond, WA), and a Hart Scientific stack base unit for temperature measurement (American Fork, UT). The temperature varied from 60 to 200 °C.

The second procedure was based on the EPA OPPTS (gas-saturation method) in which the quantity of a substance transported by a known volume of a carrier gas is determined.[29] This method is particularly suited for low vapor pressures and was used to determine the vapor pressure of the 6-2, 8-2, and 10-2 fluorotelomer alcohols at 21, 35, and 35 °C, respectively. The alcohol sample was placed in a glass thermostated tube. Gas-chromatographic grade helium (99.999%) was flowed over the solid. The flow was controlled by a flow controller on a Hewlett-Packard (now Agilent, Little Falls, DE) model 5890 gas chromatograph. Because of the adsorptive properties of the alcohol, the vapor pressure was calculated from weight loss rather than from the weight of trapped material downstream. The vapor pressure is calculated from the vapor density, W/V, by means of the equation $P = W/V \times RT/M_r$ where P is the vapor pressure in Pascals, W is the mass of transported substance in grams, V is the volume of saturated gas in cubic meters, R is the universal molar gas constant, T is the temperature in K, and M_r is the relative molecular mass.

Vapor Pressure by Gas-Phase NMR. The third method is novel and is based on gas-phase NMR, a technique for the most part neglected by chemists, that has been employed, so far only in our laboratory, to study the kinetics of a variety of reactions of organic and fluoroorganic compounds in the vapor phase at temperatures up to 400 °C with proton and fluorine detection.[30−34] In this method, the number of micromols of a proton- or fluorine-containing substance in the vapor phase in equilibrium with a small liquid pool of the same substance is measured at various temperatures relative to a much more volatile internal mass standard present in much smaller and accurately known molar amounts of about 1 mol %. Modern NMR spectrometers have adequate dynamic digital range to accurately quantify widely different integrated intensities. The vapor pressure is then obtained using the ideal gas law and the known volume of the ampule. The first application of gas-phase NMR to vapor pressure measurements was reported in our preliminary communication.[23] The experimental technique described here has been significantly refined.

The technique uses glass ampules made from sections of standard thin wall 10-mm o.d. NMR tubing, about 6 cm in

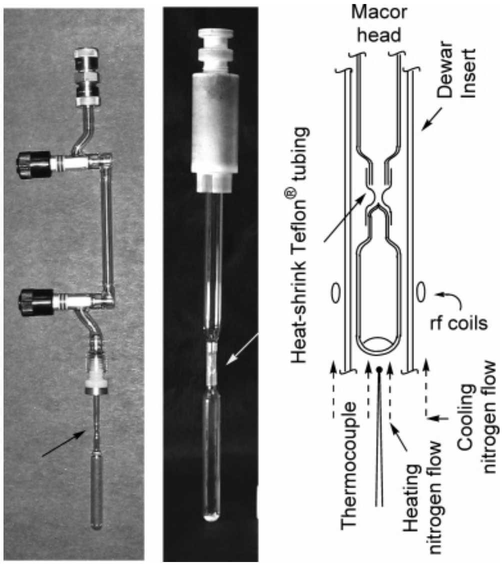


Figure 1. Left: The gas-phase NMR ampule attached to the gas buret used to introduce the internal mass standard. Center: The sealed ampule attached by means of a short Teflon sleeve to a matching 5-mm o.d. glass stub of the holding tube. The latter rests firmly in a Macor ceramic head that seals the heated compartment of the commercial high-temperature NMR probe. The ampule assembly is lowered into the magnet using a string and is not spun. The amount of sample material is chosen so that the internal pressure after complete vaporization will not a exceed a safe limit (<1.5 atm). Right: Diagram showing the gas-phase ampule in the NMR probe.

length, with 5-mm o.d. extensions to facilitate attachment to a vacuum system using an O-ring adaptor (Figure 1). The length of the ampule was chosen so as to restrict the sample to the thermostated region of the probe and to minimize temperature gradients. The ampules are now available from New Era Enterprises, Vineland, NJ. To reduce the uncertainty in the internal volume, the 5-mm o.d. extensions were constricted to an internal diameter sufficient for insertion of a syringe needle at the height where the ampule will be sealed off with a flame (see arrow in Figure 1, left panel). The internal volume for each ampule to be used (~4.0 mL) is estimated from the accurate weight of distilled water needed to fill the ampule up to a sealing mark on the constriction. The ampules are kept in a vacuum oven at ~110 °C prior to use.

For vapor pressure measurements, a quantity of substance is chosen so that at the temperature corresponding to the normal boiling point there will be a residual small pool of liquid at the bottom of the ampule (Figure 1). Liquid substances, such as 4-2 FTOH and 6-2 FTOH, are transferred into the ampules by microsyringe with elongated needles and are weighed (150−250 μmol). Substances that are solids at room temperature, such as 8-2 FTOH and 10-2 FTOH, are weighed into small vials in similar micromolar amounts, dissolved in small volumes of a volatile solvent, such as 1,1,2-trichloroethane (Freon113), and the solutions are transferred to the ampules with an elongated thin pipet. Attachment of the loaded ampules to a high-vacuum manifold equipped with a precision capacitance pressure transducer (MKS Instruments, Inc.) is made via the gas buret shown in Figure 1, having an O-ring vacuum adaptor for the ampules at one end and a vacuum O-ring union (Cajon Company) for quick attachment to the manifold at the other. The internal volume of the short piece of tubing between the two vacuum stopcocks in the gas buret (3.92 mL) was determined by vacuum techniques (expansion of an inert gas of known volume and pressure) as well as by the accurate weight of water needed to fill it. The gas buret serves to introduce into the ampule a known micromolar amount (about 1 mol %) of a volatile mass standard. Previously, we have used tetramethylsilane, TMS, for proton detection and hexafluoroethane, Freon-116, for fluorine detection.[23] The much more volatile cyclopropane (bp −32.8 °C) is used in this work to minimize coadsorption with the substance whose vapor pressure is measured (vide infra). After removal of solvents, if used, and careful degassing by freeze−pump−thaw cycling, the ampule is immersed in liquid nitrogen and is thoroughly evacuated. The stopcock from the gas buret to the ampule is then closed, and an appropriate pressure of cyclopropane is introduced into the manifold and the buret such that, when the upper stopcock of the buret is closed, the isolated cyclopropane in the known volume of the buret will correspond to about 1 mol % of the substance in the ampule. The lower stopcock of the buret is then opened to condense the cyclopropane plug into the ampule, which is then sealed off with a flame at the mark on the constricted part of its neck.

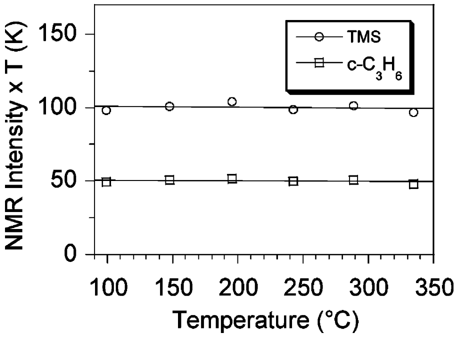


Figure 2. Plot of (NMR intensity × absolute *T*) vs temperature (°C) for the resonances of a 1:1 mol/mol mixture of tetramethylsilane and cyclopropane in the vapor phase.

The loaded sealed ampule is attached to a sample holder by means of a short piece of poly(tetrafluoroethylene) sleeve (Figure 1) and lowered into the high-temperature NMR probe (Nalorac Corporation, now part of Varian) so that only the vapor phase in the ampule is probed by the spectrometer. ^{1}H NMR spectra are acquired, at appropriate increments of temperature, from the lowest temperature giving sufficient vapor pressure for detection up to the temperature of complete vaporization. Because of the low heat capacity of the loaded ampule, temperature equilibration takes place in less than 5 min. Complete vaporization is recognized when an increment in temperature leads to a slight decrease, rather than increase, in signal intensity. This is because signal intensities in magnetic resonance are proportional to the number of nuclei being detected, increasing in our case as the vapor pressure increases but inversely proportional to the absolute temperature *T*.[35] Accordingly, as shown in Figure 2 for a test ampule containing a 1:1 mixture of TMS and cyclopropane entirely in the vapor phase, a plot of the product of the NMR integrated intensities times the absolute temperature against the temperature yields two straight lines with ordinates in the ratio of 2:1 since TMS has twice as many equivalent protons as cyclopropane.

Ideally, on the assumption that the amount of volatile mass standard adsorbed in the deliberately very small pool of liquid substance under study is a very small fraction of the total, the NMR spectra at each temperature would be carefully integrated and the integrated intensities of the resonances of the protons or fluorines associated with the substance under study would be compared, after normalization for the number of equivalent nuclei giving rise to each resonance, with the similarly normalized integrated intensity of the mass standard. All mass standards employed in this work and in the preliminary report (ref 23) give rise to a single resonance appropriate for either 12 equivalent nuclei (TMS) or 6 equivalent nuclei (cyclopropane and Freon-116). Careful scrutiny of the data, however, revealed that the above assumption was not sufficiently good and that cyclopropane coadsorbed with the telomer alcohols in significant amounts even at surprisingly elevated temperatures and thus did not report fully in the vapor phase until the telomer alcohols themselves were completely vaporized. A plot such as that in Figure 2 for cyclopropane in the presence of fluorotelomers did not become a straight horizontal line until complete vaporization of the telomers. To compensate for this coadsorption effect, three spectra were taken at a temperature where the vaporization is complete (e.g., at 300 °C or 573.1 K) and an average integrated intensity of the cyclopropane resonance was obtained, $I_{\mathrm{ave}}(573.1$ K). Since identical acquisition parameters were used at all temperatures (including precise impedance matching of the probe at each temperature), the expected integrated intensity for cyclopropane at a lower temperature T in the absence of adsorption problems, that is, if completely in the vapor phase, can be simply calculated as $I(T) = I_{\mathrm{ave}}(573.2\ \mathrm{K}) \times 573.2/T$. As the number of micromols of the mass standard in the ampule is known as well as its $1/T$ corrected integrated intensity, the micromols of the fluorotelomers in the vapor phase at each temperature can be derived by comparing the average integrated intensity of the proton resonances for the three types of protons in the fluorotelomers ($-CH_2CH_2OH$, vide infra) with $I(T)$ for the mass standard. The vapor pressure of the fluorotelomer alcohol can then be calculated using the ideal gas law and the known internal volume of the ampule. The ideal gas law gives an upper bound for the vapor pressures of the compounds studied in this way; in the presence of appreciable nonideal behavior, the true vapor pressure can only be lower than that calculated by the ideal gas law.

NMR spectra were obtained with a Varian INOVA spectrometer operating at 399.973 kHz with a wide-bore Oxford cryomagnet. The high-temperature 10-mm probe and variable temperature (VT) controller have an upper temperature rating of 400 °C and were purchased from Nalorac Corporation (now part of Varian Inc.). Since ^{19}F spin-rotation relaxation is very efficient in the gas phase, 50-ms recycle delays were appropriate and permitted rapid signal averaging (e.g., 32 transients in much less than 1 min). Proton spin-rotation relaxation is less efficient and a single pulse was used. In general, the NMR lines are broader in the gas phase than in solution, particularly for fluorines, and magnetic field homogeneity is less critical than for solution NMR; consequently, no field lock was used and the ampules were not spun.

Thermal losses in the probe necessarily lead to sample temperatures that are lower than the variable temperature (VT) controller set point. The internal temperature was calibrated with a thin thermocouple positioned in the center of a dummy ampule, identical to those used for the actual vapor density measurements except for a small hole at the end of the 5-mm stub to allow entry of the thermocouple. A temperature calibration curve was obtained by measuring over a broad temperature range the internal temperatures in the dummy ampule, positioned in the probe exactly as the actual samples, and comparing them to the controller set temperatures. The internal temperature depends on the flow rates (regulated by mass controllers for reproducibility) of the heating nitrogen gas whose temperature is being regulated by the VT controller and on that used for cooling of the peripheral space around the probe Dewar. For the flow rates used in this work, $t_{\mathrm{corrected}}$ (°C) $= t_{\mathrm{controller}}$ (°C) $- 0.0001289 \times (t_{\mathrm{controller}}$ (°C)$)^2$. The temperature error is estimated to be no more than ±2 °C.

Although the fluorotelomer alcohols under study contain both protons and fluorines, proton detection was used for vapor pressure determinations since NMR absorptions in the gas phase are narrower for protons than for fluorines and can be integrated more accurately.

Intramolecular Hydrogen Bonding Assessment. 2D HOESY NMR. The 4-2 and 8-2 fluorotelomer alcohols were studied by 2D heteronuclear Overhauser effect spectroscopy (HOESY).[36] In each case 0.10 M solutions in CD_2Cl_2 dried over 4 Å molecular sieves and containing traces of TMS and fluorotrichloromethane (Freon-11) were used. The 2D ^{19}F$-^{1}$H HOESY spectra (^{19}F observed) were acquired on a 500 MHz Bruker Avance DRX spectrometer with a ^{19}F frequency of 470.712 MHz. The pulse sequence used was Hoesyph, found in the Bruker pulse sequence library. A quad probe was used for this experiment with a ^{19}F 90° pulse of 12 μs (using 100 W amplifier) and with a ^{1}H 90° pulse of 40 μs (using a 10 W amplifier). The spectra were obtained at 30 °C using 300- and 600-ms mixing times, 10-s recycle time (because of the long relaxation times of the fluorines in solution), 1024 t_2 points, 256 scan averages, and 110 t_1 increments, with a spectral width of 30441.4 Hz in t_2 and a 3369.59 Hz spectral width in t_1, with 1H decoupling during the acquisition time. The spectrum was processed using a Gaussian function in t_2 with 1024 points and a Gaussian function in t_1 with 1024 points. The spectra were displayed in phase-sensitive mode and linear prediction was used, backward in the t_2 and forward in the t_1 dimensions.

Gas-Phase FTIR. The IR spectrum of 4-2 FTOH in the vapor phase in equilibrium with its liquid phase at room temperature was acquired using a 10-cm gas IR cell with NaCl windows and with a well containing approximately 1 mL of the liquid alcohol. Prior to the IR measurement, the cell was attached to a vacuum system and the 4-2 FTOH in the well was degassed by freeze−pump−thaw cycling. The IR spectrum of the equilibrated vapor at room temperature was obtained with a Nicolet Magna 760 FTIR spectrometer equipped with a cooled MCTB detector. 4 cm^{-1} resolution and 64 scans were employed.

Results and Discussion

Vapor Pressure of Fluorotelomer Alcohols. The vapor pressures determined by the Scott method at various temperatures up to the normal boiling point for the 6-2 and 8-2 fluorotelomer alcohols and by the gas-saturation method at close to ambient temperatures for the 6-2 (35 °C), 8-2 (21 °C), and 10-2 (35 °C) fluorotelomer alcohols are tabulated in Table S1 (Supporting Information section) and are shown graphically on a logarithmic scale in Figure 3 (white crosses and filled squares, respectively). Since the 8-2 and 10-2 fluorotelomer alcohols are solids at ambient temperature, the gas-saturation methods afford solid-phase vapor pressures.

The thermodynamic basis for interpreting the temperature dependence of the vapor pressures of liquids is the Clapeyron equation expressing a relationship between the temperature coefficient of the vapor pressure, the absolute temperature T, the molar heat of vaporization ΔH, and the volume change per mole transferred from the liquid to the vapor phase.[37] The

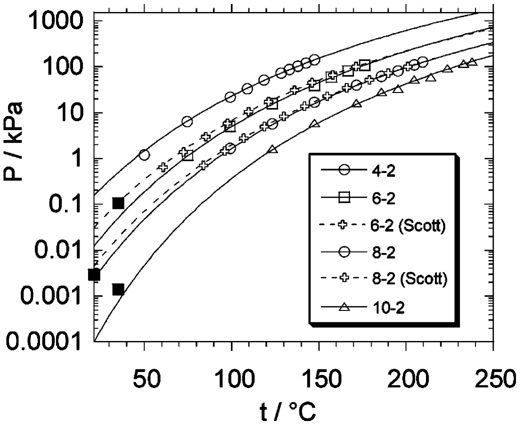


Figure 3. Plot of vapor pressure of fluorotelomer alcohols vs temperature as determined by three methods: gas-phase ^{1}H NMR, Scott method, and gas-saturation method (filled squares). Data are fit by the Antoine equation.

TABLE 1: Antoine Parameters and Extrapolated Vapor Pressures of Fluorotelomer Alcohols log P/kPa = $A - B/(t/°C + C)$

FTOH	method	A	B	C	calcd vp (Pa)	expt^a vp (Pa)
4-2	NMR	6.681	1448	172	489^b	
6-2	NMR	6.566	1506	156	50^b	108^b
6-2	Scott	6.419	1497	168	107^b	
8-2	NMR	6.412	1555	151	2^c	3^c
8-2	Scott	6.458	1623	163	4^c	
10-2	NMR	6.386	1570	130	0.7^b	1.4^b

^{a} Gas-saturation method. ^{b} At 35 °C. ^{c} At 21 °C.

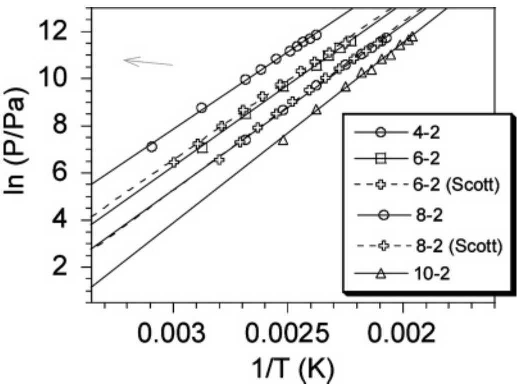


Figure 4. Plot of ln(vapor pressure) vs 1/T of the fluorotelomer alcohols. Data fit by Clausius−Clapeyron equation.

assumptions that (a) the molar volume of the vapor is much greater than that of the liquid, (b) the vapor behaves as an ideal gas, and (c) ΔH is a constant lead to the Clausius−Clapeyron equation $\log(P) = A - B/T$ where A and $B = -\Delta H/(2.3026R)$ are constants. It has long been known, however, that the temperature dependence of $\log(P)$ is linear only in a narrow temperature range, and a whole series of semiempirical equations have been proposed.[37] Of these, the Antoine equation, $\log(P) = A - B/(t + C)$, has been used extensively since it represents well the vapor pressures of most substances over large temperature intervals.[38] Indeed, an excellent fit of the data, including the low temperature determinations by the gas-saturation method, was obtained using this equation (Figure 3). Since the Antoine extrapolation below the melting point of a substance may be taken as the vapor pressure of the supercooled liquid phase, the agreement with the ambient-temperature gas-saturation value for 8-2 FTOH, which is solid at room temperatures, indicates no major difference between solid-phase and supercooled-liquid-phase vapor pressures. Accordingly, we will no longer be concerned with the distinction between solid phase and supercooled liquid phase for 8-2 and 10-2 FTOHs that are solids at room temperature.

The resulting values of the Antoine parameters are collected in Table 1 together with the extrapolated values of the vapor pressures of the fluorotelomer alcohols at ambient temperatures. The normal boiling points (vapor pressure at 101.325 kPa) of 171.5 °C and 201.3 °C were extracted for 6-2 FTOH and 8-2 FTOH. Excluding the gas-saturation values from the data to be fitted had no effect on the resulting Antoine parameters, as expected by the fact that these values are several orders of magnitude smaller than the vapor pressures at higher temperatures measured by the Scott method. It is reassuring, therefore, keeping in mind the difficulties in extrapolating exponential behavior far from the range of the measurements and that the extrapolation for a substance that is a solid at room temperature (8-2 FTOH) strictly refers to a supercooled liquid phase, that the gas-saturation points for 6-2 FTOH (35 °C) and 8-2 FTOH (21 °C) fall so close to the respective extrapolated values based on the Antoine equation (Table 1, Figure 3).

Since the vapor pressures of fluorotelomer alcohols at ambient temperatures are important for understanding their potential for atmospheric transport, the extrapolation of the vapor pressure data to these temperatures based on the Clausius−Clapeyron equation, used in ref 24, was also considered. Careful scrutiny of the ln(P) versus 1/T plot of Figure 4 shows a slight downward curvature of all the data, indicating that the data cannot be adequately represented by a straight line. Indeed, a distinct improvement in the R quality factor of the fits was obtained with quadratic functions with negative curvatures. Accordingly, the extrapolated values at ambient temperature based on the Clausius−Clapeyron equation will be higher than those based on the Antoine equation. For example, the extrapolated value of the vapor pressure for 8-2 FTOH at 21 °C on the basis of the Clausius−Clapeyron equation is 16 Pa compared to 4 Pa obtained by the Antoine fit.

Figure 5A shows the proton NMR spectrum of the vapor phase in equilibrium with a small pool of liquid 8-2 FTOH at 148 °C in an ampule charged with 73 mg (155 μmol) of the fluorotelomer alcohol and 1.5 μmol of cyclopropane. As the temperature is raised, the intensities of the 8-2 fluorotelomer alcohol resonances increase relative to that of cyclopropane as more of the fluorotelomer alcohol vaporizes (Figure 5B). There are three absorptions for the $-CH_2CH_2OH$ protons with their spin−spin interaction structures as well as a single absorption for the six equivalent protons of cyclopropane. Lower resolution is observed in the vapor phase relative to solution spectra, particularly at low internal pressures, as a result of spin-rotation relaxation effects. The $-CH_2-$ protons next to the $-OH$ group ($\delta = 3.9$ ppm) interact almost equally with the hydroxylic proton ($J = 5.8$ Hz) and with the adjacent $-CH_2-$ protons ($J = 6.4$ Hz) giving rise to a pseudo-quartet at the available resolution. The $-CH_2-$ protons next to the $-CF_2-$ group ($\delta = 2.3$ ppm) interact with two fluorines ($J = 17.8$ Hz) and with the neighboring $-CH_2-$ protons ($J = 6.4$ Hz) to yield a triplet-of-triplets structure. Finally, the hydroxylic proton ($\delta = 0.9$ ppm) shows only the already encoutered interaction with the $-CH_2$-OH methylene protons ($J = 5.8$ Hz) giving rise to a triplet. No spin−spin interaction of the hydroxylic proton spin with any fluorine spin is discernible. The presence of minimal quantities of water would broaden and wash out the triplet structure of

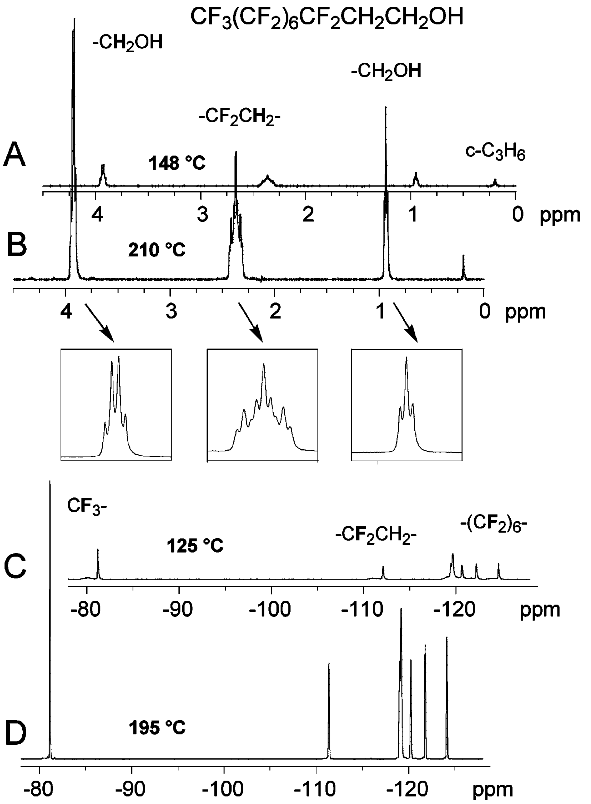


Figure 5. ^{1}H-Proton (A, B) and ^{19}F-fluorine (C, D) gas-phase NMR spectra of 8-2 FTOH at different temperatures. ^{1}H chemical shifts were measured relative to δ(H) = 0.19 ppm for cyclopropane (referenced to TMS in the vapor phase), and ^{19}F chemical shifts were measured relative to δ(F) = 0 ppm for $CFCl_3$ (F11) in the vapor phase.

the hydroxylic proton resonance as a result of intramolecular exchange. The observation of a well-resolved triplet structure for the −OH resonance is, therefore, evidence that the sample was quite free of adsorbed water.

The fluorine resonances of 8-2 FTOH behave similarly with temperature as shown in Figure 5C and 5D: they also grow in intensity as the temperature is increased until all 8-2 FTOH has entered the vapor phase. The broader lines characteristic for fluorines in the vapor phase mask any spin−spin structure and reduce the accuracy of integration compared to proton detection. Accordingly, the quantitative treatment to yield vapor pressure was carried out using proton detection.

TABLE 2: Extrapolated Vapor Pressures at 25 °C of Select Fluorotelomer Alcohols

FTOH	literature[a] (Clausius−Clapeyron) (Pa)	literature[b] (estimated by GC method) (Pa)	Scott method (Antoine) (Pa)	gas-phase NMR (Antoine) (Pa)	normal boiling point (°C)
4-2	992	1670		216	137.5[c]
6-2	713	876	44	18	173.8[c] 171.5[d]
8-2	254	227	7	4	202.0[c] 201.3[d]
10-2	144	53		0.2[e]	228.4[c]

[a] From ref 24. [b] From ref 25. [c] Gas-phase NMR using Antoine fit. [d] Scott method using Antoine fit. [e] Compare with experimental value of 1.4 Pa at 35 °C (gas-saturation method).

The number of micromoles of 8-2 FTOH in the vapor phase at each temperature can be easily determined by comparing the average integrated NMR intensity for the three protons with the 1/*T* corrected integrated intensity (see above) for the cyclopropane mass standard present in known micromolar amounts (~1 mol %). The integrated intensities must, of course, be normalized for the number of equivalent protons giving rise to each resonance (two for the CH_2 protons, one for the OH proton, and six for the cyclopropane protons). Since the internal volume of the ampule is known, the vapor pressure at each temperature can be calculated using the ideal gas law. The same procedure was followed for the 4-2, 6-2, and 10-2 fluorotelomer alcohols whose ^{1}H gas-phase NMR spectra are almost indistinguishable from that of 8-2 FTOH save for the temperature dependence of the NMR intensities. The vapor pressures determined by proton gas-phase NMR for these compounds are tabulated in Table S1 (Supporting Information) and are plotted on a logarithmic scale as a function of temperature in Figure 3 together with the Scott method and gas-saturation-method determinations for 6-2 FTOH and 8-2 FTOH. Figure 3 also shows the curves obtained by least-squares fits of the data to the Antoine equation extended to ambient temperatures. For 8-2 FTOH the calculated vapor pressure at 21 °C is 2 Pa to be compared with 4 Pa derived from the fit of the Scott method data (experimental value = 3 Pa), while for the 6-2 FTOH the calculated value at 35 °C is 50 Pa to be compared with 107 Pa derived from the Scott method data (experimental value = 108 Pa) (Table 2). The least-squares fit for the 10-2 FTOH is less straightforward than for the lower analogues as a result of the reduced curvature of the data, and the corresponding Antoine parameters (Table 1) depend somewhat on the starting values chosen for the least squares process. As with the lower homologues, the extrapolated vapor pressure at 35 °C for 10-2 FTOH is somewhat lower than the value obtained by the gas-saturation measurement at the same temperature (1.4 Pa). As mentioned above, the inadequate linear fits of the ln(*P*) versus 1/*T* plot (Figure 4) yield higher extrapolated values compared to the Antoine equation fits and will not be discussed further. Inspection of Figure 3 indicates that the NMR-derived vapor pressures are systematically somewhat lower than the Scott method measurements, resulting also in somewhat lower extrapolated values at ambient temperatures, although the agreement for the 8-2 FTOH, the purest of the samples, is quite impressive and serves as validation of the gas-phase NMR method for the measurement of vapor pressures.

In view of the foregoing, we were surprised by the results presented in ref 24, reporting vapor pressure measurements by the boiling-point method for the same series of fluorotelomer alcohols and their extrapolation to 25 °C using the Clausius−Clapeyron equation, in that they were much higher than our extrapolated values using the Antoine equation and our measured values by the gas-saturation method at ambient temperatures. The ambient-temperature vapor pressures reported in ref 25, derived by a gas-chromatographic method for the same compounds, are similarly much higher. In ref 24, the values extrapolated to 25 °C were used to judge the reliability of four environmental models to predict vapor pressures. The observation that these models consistently yielded lower vapor pressures at ambient temperature than their extrapolated values was taken as an indication that the models did not account for a putatively significant −O−H···F− intramolecular hydrogen bonding between the hydroxylic H atom and the two fluorines next to the ethanol moiety. A direct comparison of these extrapolated values at 25 °C with our gas-saturation determinations is made difficult by the slightly different temperatures used in our experiments (21 °C and 35 °C). Table 2 compares these literature values obtained by extrapolation using the Clausius−Clapeyron equation with the extrapolated values at 25 °C from our data using the Antoine equation with the parameters of Table 1.

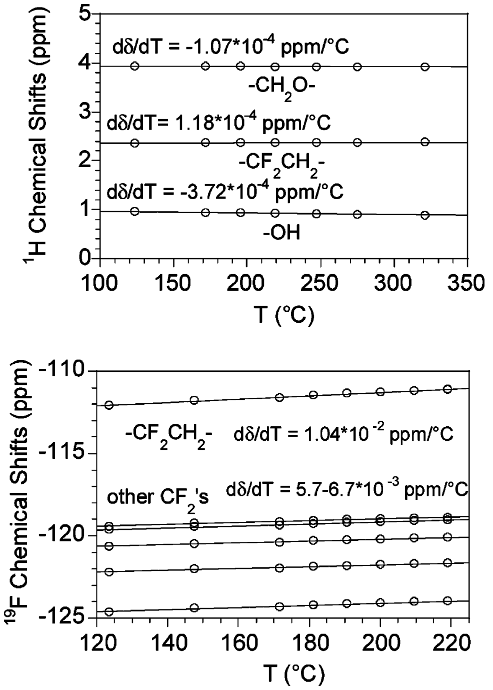
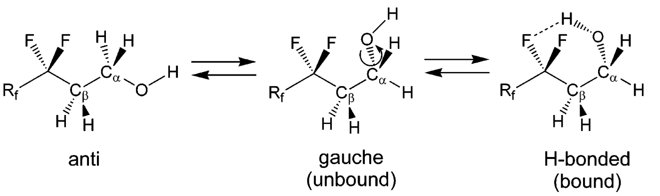


Figure 6. Plots of chemical shifts (^{1}H and ^{19}F) of 8-2 FTOH vs temperature.

Further comparison with the experimental values obtained by the gas-saturation method makes it clear that the reported literature values are overestimated.

Intramolecular Hydrogen Bonding in Fluorotelomer Alcohols. The temperature dependence of NMR chemical shifts, particularly for hydroxylic protons, if unaffected by intermolecular hydrogen bonding (high dilution limit), can provide information about intramolecular hydrogen bonding.[39] Considering just the idealized equilibrium between the unbound gauche (u) and the H-bonded (b) conformations shown below, that disregards other rotational degrees of freedom, the chemical shift of the hydroxylic proton in the two conformers will most likely have different values, δ(b) and δ(u). If the equilibration is sufficiently rapid, the observed chemical shift δ(obs) will be the average of δ(b) and δ(u) weighted by the populations of the b and u conformers, $\delta(\mathrm{obs}) = P(\mathrm{b})\delta(\mathrm{b}) + P(\mathrm{u})\delta(\mathrm{u})$. The varying populations at different temperatures will produce changes in the observed chemical shift until, at sufficiently elevated temperatures, an isotropic average is observed. The temperature dependence of the proton and fluorine chemical shifts in the gas phase for 8-2 FTOH, a byproduct of the vapor pressure measurements, is shown in Figure 6. The chemical shift of the hydroxylic proton hardly shows any change with temperature over a 250 °C temperature range providing no evidence for hydrogen bonding at these temperatures. However, a δ(obs) independent of temperature can also result if δ(u) and δ(b) should be accidentally very similar (vide infra), leading to an inconclusive result. The chemical shifts of the fluorines adjacent to the CH_2 group have the largest temperature coefficient probably because the $-CH_2-CF_2-$ bond has torsional vibrations of greater amplitude than those of the $-CF_2-CF_2-$ bonds of the stiffer fluoroalkyl chain.[40]



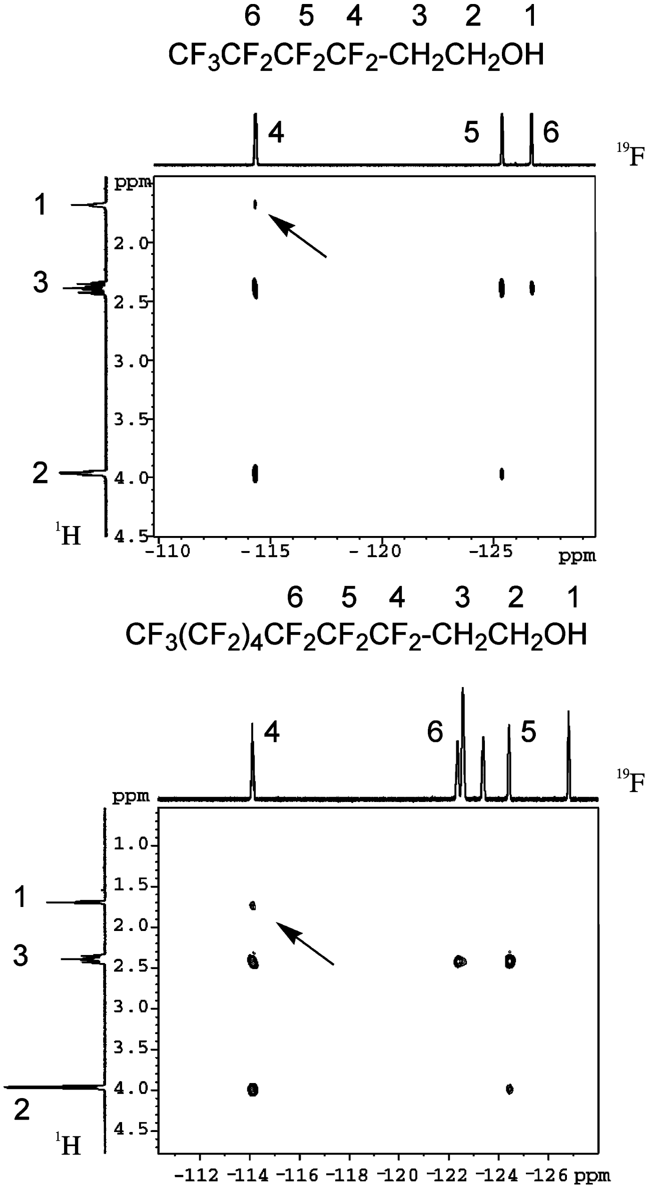
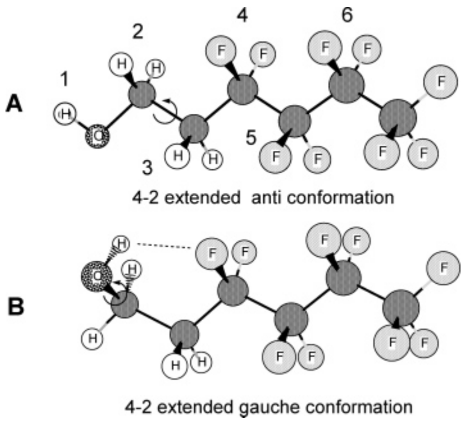


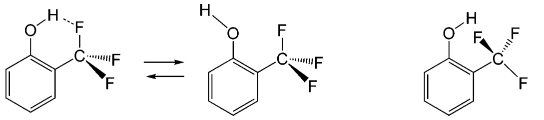
Figure 7. 2D (^{1}H, ^{19}F) HOESY NMR spectra of 4-2 and 8-2 FTOH. Arrows designate the NOE corresponding to interactions between the hydoxyl proton and the CF_2 group adjacent to the ethanol moiety.

Figure 7 shows the contour plots obtained by heteronuclear 2D Overhauser effect experiments (HOESY) on 4-2 FTOH and 8-2 FTOH in dilute methylene chloride solutions at 30 °C. The nuclear Overhauser effect provides valuable information regarding molecular dynamics and structure.[35] Since the NOE is related to $(r_{AB})^{-6}$, the average through-space distance between two dipolar interacting spins A and B can be estimated. It is apparent from Figure 7 that the smallest NOE is that labeled 1,4 (see arrows in Figure 7) between the hydroxylic proton and the fluorines of the $-CF_2-$ group attached to the ethanol moiety. Stronger and almost equal NOEs are observed for the pairs 3,4; 2,4; and 3,5 arguing in favor of an extended antiequilibrium conformation **A**. Consistent with this conformation, there are equal NOEs between the pairs 2,5 and 3,6. Thus, the heteronuclear 2D NOE experiments for both 4-2 FTOH and 8-2 FTOH fluorotelomer alcohols provide no support for appreciable contribution of a hydrogen-bonded structure such as **B** below which would be expected to give rise to a substantial NOE for the 1,4 pairs.

The IR $-O-H$ stretch vibration mode is a very sensitive indicator of hydrogen bonding. Thus, for ortho-trifluoromethylphe-



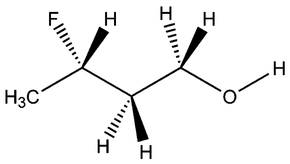
nol, one of a relatively small number of known −O−H···F− weakly hydrogen bonded systems, in isooctane solutions dilute enough so that no intermolecular association could be detected, two overlapping IR bands were observed whose relative intensities changed in the temperature range from −30 to 25 °C. [41] This behavior was the manifestation of the equilibrium, idealized below, between a hydrogen-unbonded and a hydrogen-bonded structure. The latter is appreciably populated only at subambient temperatures. The resulting $\Delta H = 1.4$ kcal/mol for this equilibrium is a measure of the strength of this hydrogen bond. More recent theoretical studies indicated a preference of the same small magnitude for a bifurcated cyclic structure idealized below.[42]

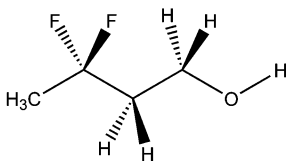


In contrast with the above, the IR spectrum of the vapor phase of 8-2 FTOH in equilibrium with its liquid phase at ambient temperature (Figure 8) showed no indication of a second O−H stretch vibrational band that might result from an appreciable population of a similarly hydrogen-bonded structure as idealized in structure **B** above.

Ab Initio Computation of Intramolecular Hydrogen Bonding in Fluorotelomer Alcohols. To further elucidate the potential role of intramolecular hydrogen bonding in fluorotelomer alcohols, we performed an extensive series of ab initio quantum chemical calculations. Hydrogen bonding is ubiquitous in the chemistry of solvated and condensed-phase systems and plays a critical role in determining the structure of biological molecules.[43] For this study, we used density functional theory (DFT) as described in the Supporting Information.

Before performing calculations on larger, highly fluorinated systems, we studied two small sparsely fluorinated molecules to see if any evidence of −OH···F− hydrogen bonding exists. The prototype species studied were 3-fluorobutan-1-ol and 3,3-difluorobutan-1-ol sketched in anticonformation below.





Each of these structures, and all other linear fluoro alcohols, exist in a variety of rotational conformations. Of critical concern for the current problem are the anti and gauche conformations, corresponding to rotation about the $C_\alpha-C_\beta$ single bond, illustrated below by Newman projections. The gauche conformation brings a fluorine atom and the hydroxyl group into close proximity and affords the best chance of forming an intramolecular −OH···F− hydrogen bond.

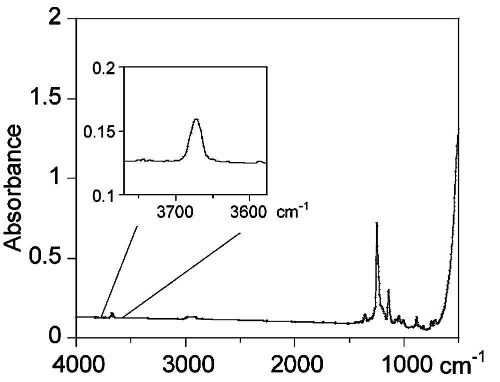
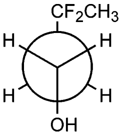


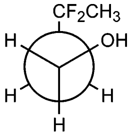
Figure 8. Gas-phase FTIR spectrum of 4-2 FTOH in equilibrium with its liquid phase at 25 °C. The inset is an expansion of the region of absorbance for O−H stretches.

TABLE 3: Relative Enthalpies[a] (kcal/mol) of the Three Critical Conformations of 3-Fluorobutan-1-ol, 3,3-Difluorobutan-1-ol, 2-2 FTOH, and 4-2 FTOH

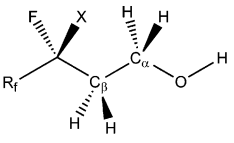
species	anti	gauche	bonded
3-fluorobutan-1-ol	0	+2.65	−0.92
3,3-diflurobutan-1-ol	0	+1.74	−0.71
2-2 FTOH	0	+1.03	−0.29
4-2 FTOH	0	+1.08	−0.34

[a] Calculational method used B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p). Enthalpies reported at 298.15 K and 1 atm.

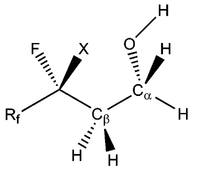




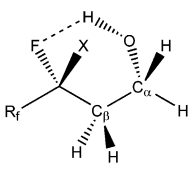
Below are sketched the three important molecular conformations for linear fluorotelomer alcohols in which X is either H or F. Structure a shows the extended anti form which a priori is expected to be the lowest energy conformation. Structure b shows the gauche conformation related to the anti form by a 120° rotation around the $C_\alpha-C_\beta$ single bond. Finally, structure c shows the likely conformation of the proposed hydrogen-bonded six-membered ring structure. In the rest of this discussion, we will refer to these conformations as anti, gauche, and bonded, respectively.



(a)
anti



(b)
gauche



(c)
bonded

In Table 3 are listed the calculated relative enthalpies of these three conformations of 3-fluorobutan-1-ol and 3,3-difluorobutan-1-ol. For both molecules, and in all subsequent tables, the reported enthalpies are relative to the anti conformation. The quoted values are ideal gas enthalpy differences at 298.15 K and 1 atm corrected for zero-point energy differences.

As Table 3 shows, the hydrogen-bonded conformation (bonded) is the lowest energy state, that is, a hydrogen bond is predicted to exist, and, as expected, the gauche form is the least stable conformation. The −C−F···H−O− hydrogen bonds are weak. A sensible definition of the bond strength is the calculated enthalpy of the bonded conformation relative to that of the gauche form. On this measure, the calculated bond strength of the singly fluorinated system is 3.57 kcal/mol, and in the doubly fluorinated system it is 2.45 kcal/mol.

Our calculations on prototype systems encouraged us to examine more representative systems. Ideally, we would perform calculations for the molecules of particular interest to atmospheric scientists, such as 8-2 FTOH, but calculations on such large systems are computationally tedious because of the large number of molecular electrons. In any case, such calculations are unnecessary. As the perfluorinated tail lengthens, the hydrogen-bond strength in the six-membered ring structure will quickly stabilize to a value that is independent of the length of the tail.

We performed calculations for two fluorotelomer alcohols: 2-2 FTOH and 4-2 FTOH. Table 3 shows the calculated relative enthalpies for the three critical conformations. The trends we observed for the prototype systems remain unaltered. The hydrogen-bonded conformation is the lowest energy state and the gauche form is the least stable conformation. The −OH···F− hydrogen bonds are now very weak. For 2-2 FTOH the bond strength is 1.32 kcal/mol and for 4-2 FTOH it is 1.42 kcal/mol consistent with the claim that the bond strength quickly becomes independent of chain length. Armed with these results, we may confidently predict that the higher FTOHs will have very weak hydrogen bonds of the order of ∼1 kcal/mol. FTOHs, like their nonhalogenated analogues, have significant intermolecular −O−H···O hydrogen bonding. For exampe, the intermolecular hydrogen-bond strength of ethanol dimers is ∼5 kcal/mol.[44] Thus, *inter*molecular hydrogen bonding will completely dominate *intra*molecular hydrogen bonding for FTOHs.

Proton NMR Chemical Shifts. We also calculated ^{1}H NMR chemical shifts for all four species studied in the previous section. For comparison with the experimental results for 8-2 FTOH reported in the section on gas-phase NMR, we will discuss the calculated values obtained for 4-2 FTOH, although the results obtained for 2-2 FTOH are essentially identical. The NMR shielding tensors and absolute chemical shifts were calculated using the gauge-independent atomic orbitals (GIAO) method.[45] The calculations were performed with B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p), and the details are summarized in the Supporting Information.

Tables S1−S3 of the Supporting Information contain the calculated proton shifts for the bonded, anti, and gauche conformations, respectively (cf. structures c, a, and b above, $X = F$, $R_f = C_3F_7$). Examination of these tables shows that the agreement between theory and experiment is exceptionally good and that the calculated proton shifts vary little among the three conformations. The average proton shifts for the $-CH_2O-$ group vary from a minimum of 4.08 ppm in the bonded state to a maximum of 4.22 ppm in the gauche conformation (∼4.0 ppm experimentally, Figure 4). For the $-CF_2CH_2-$ protons, the average computed shifts vary from 2.30 ppm in the bonded state to 2.44 ppm in the anti conformer (∼2.4 ppm experimentally, Figure 6). The largest change is for the hydroxyl proton H that varies from 0.38 to 1.35 ppm (∼1.0 ppm experimentally, Figure 6). The variation is very modest and rules out the use of temperature dependence of the observed proton shifts to quantify the relative occupation of each state.

High-level ab initio calculations do show a very weak intramolecular hydrogen-bonding interaction in fluorotelomer alcohols of about 1 kcal/mol. With such small enthalpy differences, the hydrogen-bonded conformations cannot be preferentially populated by any appreciable extent relative to unbound conformations at ambient temperatures to be of any consequence as regards vapor pressure and atmospheric transport.

In conclusion, we have shown that the vapor pressures of fluorotelomer alcohols at ambient temperature are in fact significantly lower than previously reported and that intramolecular hydrogen bonding is very weak and unlikely to affect the volatility. These results, as well as the highly sorptive nature of fluorotelomer alcohol,[46] must be taken into account in assessing the potential for atmospheric transport for these compounds.

Supporting Information Available: Table of vapor pressures of fluorotelomer alcohols *n*-2 FTOH ($n = 4, 6, 8, 10$) at various temperatures determined by three independent method, details of the ab initio computations, proton NMR chemical shifts, a table of computed proton chemical shifts for bonded conformation of 4-2 FTOH, a table of computed proton chemical shifts for bonded anti conformation of 4-2 FTOH, a table of computed proton chemical shifts for gauche conformation of 4-2FTOH, and supporting references. This material is available free of charge via the Internet at http://pubs.acs.org.

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