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With Water and Substituted Diethyl Ethers.
Chemical Ionization Mass Spectrometric
Determination of the Proton Affinity of
 $(\text{CF}_3\text{CH}_2)_2\text{O}$.

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Abstract

BF_3 was cocondensed with H_2O , D_2O , $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{CF}_3\text{CH}_2)_2\text{O}$, and $(\text{C}_2\text{F}_5)_2\text{O}$ in excess argon at 15 K. Infrared spectra of BF_3 /water isolated in solid argon provided a more complete analysis of the $\text{BF}_3\text{—H}_2\text{O}$ complex than previously published. Infrared spectra of the matrices showed a definite Lewis acid-base interaction between BF_3 and diethyl ether; a weak but definite interaction with bis(2,2,2-trifluoroethyl)ether, and no observable interaction with perfluoroethyl ether. Thus, the ether data indicate a clear trend between strength of interaction with BF_3 and the degree of F substitution. To support and explain the emerging relationship between interaction strength and the basicity of the oxygen-containing molecule, the proton affinity of $(\text{CF}_3\text{CH}_2)_2\text{O}$ was measured using chemical ionization mass spectrometry. The implications of the results for lubricant/metal oxide surface interactions will be discussed.

Introduction

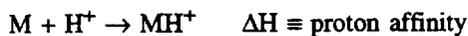
The chemistry of perfluoroalkyl ethers has come under increasing study recently, because of their application to lubrication of computer magnetic media and spacecraft devices.^{1,2} The behavior of commercial fluids, and model compounds that mimic their chemistry, has been studied both theoretically^{3,4} and experimentally for exposure to the influence of electrons,⁵ Lewis acids,⁶⁻⁹ metal oxides,^{9,10} and bare metal surfaces.^{11,12} Much attention has been given to the catalytic decomposition of perfluoroalkyl ethers which occurs when they are heated in the presence of metal oxides or halides. The effectiveness of the surfaces in catalyzing the decomposition is a strong function of the fluoroether's structure. A number of workers have observed that the

presence of an -O-CF₂-O- (acetal) linkage greatly enhances their reactivity towards catalyzed breakdown by metal oxides.^{8,13}

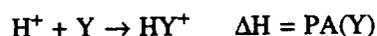
The postulated mechanisms for this catalyzed breakdown usually involve an acid-base interaction between the surface metal ions and the lone pairs on the fluoroether oxygen atoms. This is followed by chain scission. The most complete studies to date have been carried out by Kasai et al.⁷⁻¹⁰ In an elegant series of experiments, they used ¹⁹F NMR and mass spectrometry to study the Lewis acid-catalyzed breakdown of several perfluoroethers of different structures. By relating the structures of the particular perfluoroethers to that of their breakdown products, the authors produced a mechanism which explains not only the identity and distribution of the decomposition products, but also how their reactivities relate to their structures.

The initial step in the Kasai mechanism, as well as that of most other mechanisms advanced, is the donation of electron density from oxygen atoms in the chain to one or more acidic metal atoms on the Lewis acid surface. Although this is a well-established process for hydrocarbon ethers, one expects that for perfluoroethers the oxygen atoms will exhibit a much lower basicity and therefore vulnerability to attack. Alternate mechanisms which do not involve Lewis acid attack on the oxygen atoms have been proposed. Zehe and Faut⁸ studied the catalyzed breakdown of commercial fluids by α -Fe₂O₃, and proposed a mechanism involving acidic attack on the nonbonding electrons on the fluorine atoms, followed by fluorine abstraction to yield a stable carbenium species. Yates et al.¹⁴⁻¹⁶ used TDS, HREELS, and transmission IR to study adsorption and decomposition of hydrocarbon ethers and (CF₂H)₂O on planar and powdered Al₂O₃. They observed decomposition to occur for (CF₂H)₂O in contact with powdered Al₂O₃, even after pre-adsorbing pyridine to block Lewis acid sites. They concluded that Lewis acid sites were not involved in the reaction, and postulated as the first step in the decomposition a nucleophilic attack by surface oxygen on a carbon atom in the ether.

The Lewis basicity of a molecule is one indicator of its propensity to participate in acid-base chemistry. A rough measure of the Lewis basicity of a molecule is the proton affinity (PA), the energy given off as a molecule accepts a proton in the gas phase:



Proton affinities are usually stated as positive numbers, although it is understood that these reactions are exothermic. One method used to qualitatively determine proton affinities is by using chemical ionization mass spectrometry,¹⁷ whereby a protonated reactant of known proton affinity is mixed with a reactant of unknown proton affinity:



Chemical ionization mass spectrometry assumes that if the combined reaction occurs to any measurable extent, $\Delta\text{H}_{\text{tot}} < 0$, and so by evaluating the extent of these reactions in the gas phase by mass spectrometry for a set of known $\text{PA}(\text{X})$ (where X represents several molecular species), the unknown proton affinity for species Y can be estimated.

Infrared matrix-isolation spectroscopy has been used successfully for producing and studying reaction complexes, including Lewis acid-base adducts. The technique has been applied by Ault¹⁸⁻²³ to the study of a large number of Lewis acid-base complexes, both strongly and weakly bound. Strong Lewis acids such as BF_3 and SO_3 have been cocondensed at high dilution with weak Lewis bases, and complexation observed through shifts in the measured vibrational frequencies. With a given base, rough correlations have been observed between the strength of the acidity or basicity and the measured spectral shifts.

In this paper, we describe the determination of the proton affinity of $(\text{CF}_3\text{CH}_2)_2\text{O}$ by chemical ionization spectrometry, as well as the application of matrix-isolation spectroscopy to the liquid lubricant breakdown problem. The matrix-isolation experiments involved the co-condensation of the strong Lewis acid BF_3 with water and with a number of fluoroethers, to model poly(perfluoroether) lubricant/metal oxide interactions.

Experimental

Chemical ionization mass spectrometry of $(\text{CF}_3\text{CH}_2)_2\text{O}$ was performed on a Finnigan TSQ-45 gas chromatograph/mass spectrometer using its standard CI sample volume with a filament as the electron source. The reagent gas (H_2O , CH_2O , and CH_3OH) was introduced at a pressure sufficient to form a stable discharge,

the $(\text{CF}_3\text{CH}_2)_2\text{O}$ was introduced, and the mass spectrum was measured and evaluated for the presence of $(\text{CF}_3\text{CH}_2)_2\text{OH}^+$.

The matrix isolation apparatus used in this study has been previously described.²⁴ Briefly, a cryogenic sampling apparatus was constructed around an APD Displex model CSW-202 closed-cycle helium cryostat. A gold-plated copper octagon was attached to the end of the cold finger of the cryostat, surrounded by an aluminum heat shield, and enclosed in a rectangular vacuum system. The eight sides of the copper octagon were polished and acted as sample deposition surfaces. The surfaces routinely reached 15 K. Sample vapors were introduced into the vacuum system via stainless steel tubing and were regulated with Granville-Phillips high precision needle valves. The pressures of the vapors in the delivery tubes were monitored using thermocouple gauges. The estimated molar ratio of reactants and matrix gas was determined using a quartz crystal microbalance mounted in one of the sides of the octagon.

Deposition onto a clean surface typically lasted 30 min to 2 hr. After deposition, the cold finger was rotated 180° and the infrared spectrum was measured by reflection through the deposited matrix and off the gold-plated surface using a Nicolet 5DX Fourier transform infrared spectrometer at 2 cm^{-1} resolution. Five hundred scans were measured and averaged.

Purified H_2O was obtained by distillation and triple filtration using a Barnstead NANOpure water filtration system. CH_3OH (JT Baker, Ultima grade), para- CH_2O (Matheson), D_2O (ICN, 99.8%), BF_3 (Aldrich, 99.5+%), $(\text{C}_2\text{H}_5)_2\text{O}$ (Fisher, reagent grade), $(\text{CF}_3\text{CH}_2)_2\text{O}$ (PCR, Inc., 97+%), $(\text{C}_2\text{F}_5)_2\text{O}$ (Strem, Inc., 97%), and Ar (AGA, 99.9995%) were used without further purification. CAUTION: BF_3 is a highly toxic, moisture-sensitive gas; only small quantities should be used at a time, under a fume hood. CAUTION: $(\text{CF}_3\text{CH}_2)_2\text{O}$ is a convulsant and should be used only in adequate ventilation or in a fume hood.

Results

Chemical Ionization Mass Spectra of $(\text{CF}_3\text{CH}_2)_2\text{O}$ $(\text{CF}_3\text{CH}_2)_2\text{O}$ vapor was introduced into stable discharges of H_2O , CH_2O , or CH_3OH and the mass spectra were monitored for the presence of $(\text{CF}_3\text{CH}_2)_2\text{OH}^+$. The $(\text{CF}_3\text{CH}_2)_2\text{O}/\text{H}_2\text{O}$ discharge showed a peak at mass 183, due to the $(\text{CF}_3\text{CH}_2)_2\text{OH}^+$ ion. Neither $(\text{CF}_3\text{CH}_2)_2\text{O}/\text{CH}_2\text{O}$ nor $(\text{CF}_3\text{CH}_2)_2\text{O}/\text{CH}_3\text{OH}$ discharges yielded any mass 183 peaks.

Matrix FTIR Spectra When BF_3 was cocondensed with H_2O in excess Ar at 15 K, new absorptions were measured in the infrared spectrum. Figures 1 and 2 show selected regions of the IR spectra for each reactant individually and then deposited together in the same matrix. In Figure 1, a strong new absorption is noted at 3730.0 cm^{-1} , in the O-H stretching region. A less intense and broader absorption appeared at 3551.2 cm^{-1} , also in the O-H stretching region. In Figure 2, a series of broad, medium-intensity absorptions are seen at 1314.6 , 1283.9 , 1264.7 , and 1251.9 cm^{-1} . A doublet occurred at 874.5 and 851.5 cm^{-1} , and strong and sharp absorptions were seen at 691.5 and 664.0 cm^{-1} , in the vicinity of the ν_2 mode of BF_3 .²⁵ Finally, a new peak at 654.9 cm^{-1} appeared in this same region.

Figure 3 shows portions of the infrared spectra measured for BF_3 cocondensed with D_2O in excess argon. New absorptions were measured corresponding to those detected in the $\text{BF}_3/\text{H}_2\text{O}$ experiments, but shifted due to isotopic substitution. In addition to the new features at 690.9 and 664.5 cm^{-1} shown in Figure 3, absorptions at 2721.3 , 2684.0 , and 2629.7 cm^{-1} appeared in the O-D stretching region, and new absorptions in the 1310 to 1260 cm^{-1} range appeared again as well as absorptions at 870.6 and 851.6 cm^{-1} . However, there was no absorption corresponding to the previous band at 654.9 cm^{-1} for $\text{BF}_3/\text{H}_2\text{O}$.

BF_3 was cocondensed with diethyl ether in excess Ar. When the infrared spectrum was measured, new absorptions were seen. Figure 4a shows the wavelength region 1300 to 600 cm^{-1} for BF_3 in Ar, illustrating the BF_3 bending mode²⁵ (split into two absorptions following the natural 20%/80% $^{10}\text{B}/^{11}\text{B}$ isotopic abundance of boron). Several new absorptions appeared, indicated by the features in Figure 4c marked with an asterisk. The absorptions appearing at 1241.1 and 1207.6 cm^{-1} are very close to the positions reported by Hunt and Ault¹⁹ for the antisymmetric B-F stretches of the $\text{BF}_3\text{—O}(\text{CH}_3)_2$ complex. A broad absorption appearing at 875.8 cm^{-1} corresponds to the symmetric C-O stretch of the ether moiety. A new absorption at 762.0 cm^{-1} can be assigned to a symmetric B-F stretch; a very weak feature at 796.8 cm^{-1} could be the ^{10}B counterpart.

When BF_3 is condensed with $(\text{CF}_3\text{CH}_2)_2\text{O}$, new absorptions appear; these new absorptions are illustrated in Figures 5c and 6c. All of the new absorptions shown in Figure 5, occurring at 1229.6 , 1220.0 , and 1116.1 cm^{-1} , appeared very close to the infrared absorptions of the parent molecules. Another absorption, not shown in the figures and occurring at 1330.0 cm^{-1} , also appears to be a shift of a parent fluoroether absorption. Figure 6a shows the infrared spectrum of BF_3 between 740 and 600 cm^{-1} , where the out-of-plane bending

vibration of the planar BF_3 molecule absorbs. $^{10}\text{BF}_3$ absorbs at 705 cm^{-1} , and $^{11}\text{BF}_3$ at 678 cm^{-1} . These absorptions show an approximate intensity ratio expected for naturally-occurring boron. Figure 6c shows the same region for the codeposited $\text{BF}_3/(\text{CF}_3\text{CH}_2)_2\text{O}$ sample and indicates two broad absorptions at 694.9 and 668.0 cm^{-1} that are present only upon cocondensation.

When BF_3 was condensed with $(\text{CF}_3\text{CF}_2)_2\text{O}$ in excess Ar, no new absorptions were observed. However, BF_3 and $(\text{CF}_3\text{CF}_2)_2\text{O}$ were cocondensed at 15 K without Ar; a portion of the infrared spectrum of the neat cocondensation is shown in Figure 7. No new absorptions appeared upon cocondensation; but, upon briefly annealing the sample to $\sim 105\text{ K}$, several new absorptions did appear in the C-F and C-O stretching region as shown in Figure 7b. These absorptions were reproducible over several depositions and appeared at about the same annealing temperature for all codeposited samples. The three strongest absorptions appeared at 1189 , 1170 , and 1094 cm^{-1} , and as shown in Figure 7, appear to be perturbations of the strong, broad infrared absorptions of the parent molecules as opposed to a Lewis acid-base complex. No new absorptions were detected in the BF_3 bending region, where evidence of perturbations of the BF_3 moiety were previously evident.

Discussion

Chemical Ionization Mass Spectra The molecular ion for $(\text{CF}_3\text{CH}_2)_2\text{O}$ appears at 182 amu , with the protonated form having a mass of 183 amu . Mass spectra of $(\text{CF}_3\text{CH}_2)_2\text{O}$ showed only a very small peak at mass 183 , due to the natural abundance of ^{13}C in the molecules. The most intense mass peak occurred at mass 113 , corresponding to the loss of an CHF_3 moiety from the protonated molecule. The second-most intense mass peak occurred at 163 amu , corresponding to the loss of HF from the protonated molecule. The $(\text{M}+1)^+$ peak at mass 183 is $<3\%$ of the intensity of the strongest peak at mass 113 . This illustrates one of the challenges of measuring the mass spectra of protonated fluorocarbons: the facility with which stable fluorine species split off from the energized, protonated molecule.

The proton affinities of H_2O , formaldehyde, and methanol are 173.0 , 177.2 , and 184.9 kcal/mol , respectively.¹⁷ The mass spectra of $(\text{CF}_3\text{CH}_2)_2\text{O}$ using H_2O as a CI reagent shows a strong $(\text{M}+1)^+$ peak at 183 mass units, revealing that efficient protonation of the ether occurs by H_3O^+ . For $(\text{CF}_3\text{CH}_2)_2\text{O}$ in either a formaldehyde or methanol discharge, however, no mass 183 peak was detected other than what results from the natural isotopic abundance of ^{13}C . Thus, these "bracketing" experiments show that the proton affinity of

bis(2,2,2-trifluoroethyl)ether is between that of H₂O (173.0 kcal/mol) and formaldehyde (177.2 kcal/mol). Since the proton affinity of the bis(2,2,2-trifluoroethyl)ether is very close to that of H₂O, one would expect that the complexes formed between BF₃ and H₂O or (CF₃CH₂)₂O be of similar strength. A discussion of the two sets of results will be given below.

Matrix Isolation Studies. BF₃ + H₂O H₂O and D₂O were included in this study because a complex with BF₃ was known to exist,²⁶ and its matrix-isolated spectrum had been previously reported, albeit in an abbreviated fashion.¹⁹ The known proton affinity of H₂O would also allow the BF₃—H₂O complexes to serve as test cases for any proton affinity versus vibrational frequency shift relationship that exists for the family of BF₃-ether complexes to be studied.

Hunt and Ault had previously reported¹⁹ spectra of matrix-isolated BF₃—H₂O, but their report concentrated on the region from 1200 to 1300 cm⁻¹ where it was expected that the B-F stretches of a complexed BF₃ species would absorb. They reported absorptions at 1313, 1285, and 1241 cm⁻¹ which they assigned to antisymmetric B-F stretches of the complex. The work presented here confirms the appearance of these new absorptions, as well as their assignment to the BF₃ moiety by the fact that they shift very little upon interaction with D₂O. However, several other absorptions appear upon formation of BF₃—H₂O. A strong absorption at 3730.0 cm⁻¹ is assigned to the asymmetric O-H stretch of the complexed H₂O molecule, and the absorption at 3551.2 cm⁻¹ is assigned to the symmetric O-H stretch of the same species. An absorption at 874.5 cm⁻¹, slightly shifted upon deuteration to 870.6 cm⁻¹, is assigned to the activated symmetric stretch of the BF₃ moiety, which for the free molecule is infrared-inactive and occurs at 888 cm⁻¹.²⁵ Further similar assignments can be made for the BF₃—D₂O complex; these assignments are listed in Table I.

But the most informative absorptions of the BF₃—H₂O complex occur in the long wavelength end of the spectrum, in the region of the ν₂ mode of the BF₃ molecule (Figures 2 and 3). The two new absorptions at 691.5 and 664.0 cm⁻¹ correspond exactly in relative position and relative intensities to the ν₂ doublet of molecular BF₃. This suggests that the interaction between BF₃ and H₂O is weak, and that BF₃ has not significantly deviated from planarity. In other words, a classic Lewis acid-base adduct has not been formed; instead, a sort of "perturbation complex" is indicated. We suggest that the H₂O molecule does indeed interact with BF₃, but that

the molecular complex so formed is indistinct and weak, and not strong enough to distort the local BF_3 molecular symmetry.

Finally, the appearance of a strong absorption at 654.9 cm^{-1} would be consistent with an intramolecular B-O stretch, but it would be too high in energy for such a weak intermolecular interaction, as is postulated based on the evidence discussed above. Its disappearance for $\text{BF}_3\text{-D}_2\text{O}$ spectra confirms that it is indeed not a B-O stretch. If the absorption had indeed shifted out of range of the spectrometer upon deuteration of water, the only conceivable motion that would account for its presence would be a type of wag or libration of the H_2O moiety attached to BF_3 . Aquo complexes are known to have motions of this sort, occurring in this spectral range.²⁵ It is tentatively assigned as such, and normal coordinate analysis and ab initio investigations of this system are being pursued to identify the nature of this absorption.²⁷

BF_3 + ethers Under similar conditions of deposition in cryogenic argon matrices, the BF_3 /diethyl ether system produced strong, new absorption peaks, the BF_3 /bis(2,2,2-trifluoroethyl)ether system produced only slight shifts in the parent molecular absorptions, and the BF_3 /perfluorodiethyl ether system produced no new absorptions and no shifts in the parent molecule absorptions. This indicates a clear trend between the degree of fluorine substitution on the ether and the strength of interaction with the Lewis acid BF_3 . A reasonable explanation would be the decreasing basicity which accompanies fluorine substitution on the ether, leading to a lower proclivity to interact with the acid.

$\text{BF}_3 + (\text{C}_2\text{H}_5)_2\text{O}$ New absorptions found when diethyl ether was cocondensed with BF_3 indicate that a Lewis acid-base complex was formed. Several of the new absorptions appeared in spectral regions that were similar to new vibrations in BF_3 /dimethyl ether samples reported by Hunt and Ault.¹⁹ The new absorptions at 1241.1 and 1207.6 cm^{-1} are assigned to the antisymmetric B-F stretching vibration of the BF_3 moiety. The 875.8 cm^{-1} peak appears in the expected region for the symmetric C-O stretching vibration, and the absorptions at 796.8 and 762.0 cm^{-1} coincide with the symmetric B-F stretch. These two absorptions have the correct approximate 1:3 intensity ratio, suggesting assignment to a vibration involving a boron atom. No boron isotopic splitting was seen for either the 1241.7 or the 1207.6 cm^{-1} absorption. The assignments to $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ echo those of the dimethyl ether/boron trifluoride matrix spectra, which indicated similar results.¹⁹ The absorptions of $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ and their approximate assignments are listed in Table II.

The pattern of these product absorptions, when compared to those from previous detailed studies, indicate that a Lewis acid-base complex is being formed spontaneously between BF_3 and $(\text{C}_2\text{H}_5)_2\text{O}$ in argon matrices. Its formation is not surprising, given that the gas-phase proton affinity of dimethyl ether (with which a BF_3 complex is formed spontaneously) is 192.1 kcal/mol, as compared to 200.4 kcal/mol^{17,28} for diethyl ether. Several papers by Ault et al.¹⁹⁻²¹ show that the base proton affinity is a good indicator of the strength of interaction between an acid and a series of bases, where the strength of interaction is inferred from the shift of a vibration of the acid.

$\text{BF}_3 + (\text{CF}_3\text{CH}_2)_2\text{O}$ When BF_3 was cocondensed with bis(2,2,2-trifluoroethyl)ether, new absorptions were again detected. These new absorptions are listed in Table III. However, instead of appearing in spectral regions characteristic of a Lewis acid-base interaction, the new absorptions appear to be only slightly shifted from the absorptions of the parent molecules; they are assigned as such in Table III. This suggests that the interaction between BF_3 and $(\text{CF}_3\text{CH}_2)_2\text{O}$, while apparent, is weak.

We measured the proton affinity of $(\text{CF}_3\text{CH}_2)_2\text{O}$ by chemical ionization mass spectrometry as approximately 175 kcal/mol. This is approximately 25 kcal less than the proton affinity of diethyl ether, which is 200.4 kcal/mol;¹⁷ it is therefore not surprising that $(\text{CF}_3\text{CH}_2)_2\text{O}$ interacts more weakly with BF_3 . The presence of the strong electron-withdrawing fluorine atoms on the ether serves to pull electron density off the oxygen atom, making the overall molecule less basic. This trend is supported by the weak interactions between $(\text{CF}_3\text{CH}_2)_2\text{O}$ and BF_3 in cryogenic argon matrices. This weak interaction is best illustrated by the 10 cm^{-1} shifts in the out-of-plane bending vibrations of $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$ shown in Figure 6. The same red shift in energy as well as the proper intensity ratio of the absorptions at 694.9 and 668.0 cm^{-1} supports the idea of a mutually perturbing influence of the dopant molecules, not the formation of a new *bona fide* molecular complex. The fact that the only BF_3 mode that shows any perturbation is the out-of-plane bending mode suggests that the BF_3 unit is interacting with the ether in an orientation that is perpendicular to the BF_3 plane. Unfortunately, due to presence of C-O and C-F absorptions in a similar region, the exact interaction point on the ether molecule is indeterminate; while an O-atom interaction is probable, interaction through the electron-rich fluorine atoms cannot be ignored as a possibility. A detailed vibrational assignment of $(\text{CF}_3\text{CH}_2)_2\text{O}$ would be useful in interpreting the details of the interaction spectra; such an analysis is pending.²⁹

A quick comparison of $\text{BF}_3\text{---H}_2\text{O}$ and $\text{BF}_3\text{---}(\text{CF}_3\text{CH}_2)_2\text{O}$ is warranted. Based on the infrared spectra, especially the region 700 to 650 cm^{-1} , both Lewis bases perturb BF_3 , acting as very weak Lewis bases and not forming true acid-base adducts. The proton affinity of H_2O is 173.0 kcal/mol ,¹⁷ we have measured the proton affinity of $(\text{CF}_3\text{CH}_2)_2\text{O}$ as $\sim 175\text{ kcal/mol}$. The data presented here show that H_2O shifts $\nu_2(\text{BF}_3)$ by $\sim 13\text{ cm}^{-1}$ and $(\text{CF}_3\text{CH}_2)_2\text{O}$ shifts $\nu_2(\text{BF}_3)$ by $\sim 10\text{ cm}^{-1}$. The similar spectral shifts indicate that similar complexation strengths are being realized. The proximity of the proton affinities of water and bis(2,2,2-trifluoroethyl)ether confirm that similar spectral shifts should indeed be observed.

$\text{BF}_3 + (\text{C}_2\text{F}_5)_2\text{O}$ When BF_3 was cocondensed with perfluorodiethyl ether in excess argon, no new infrared absorptions were detected. Even the ν_2 vibration of BF_3 , shown above to be sensitive to weak interactions, showed no change upon codeposition. While it is certainly possible that new infrared-active vibrations were too weak to be detected, given the pattern of interactions already discussed it is more probable that there is no interaction between BF_3 and $(\text{C}_2\text{F}_5)_2\text{O}$ under these conditions. The increased electron-withdrawing capacity of more fluorine substituents on the ether is expected to severely lower the proton affinity of the ether, possibly enough to prevent any sort of detectable interaction in these circumstances.

This lack of reactivity is not unique; Ault¹⁸ reported no Lewis acid/base adducts forming between SiF_4 and any oxygen-containing bases. Similar experiments reacting SiF_4 with PH_3 , which has a proton affinity similar to that of dimethyl ether,^{17,18,30} also showed little interaction. It appears that some minimum relative basicity is necessary in order to form Lewis acid-base complexes in cryogenic matrices. Attempts have been made³¹ to measure the gas-phase protonation of perfluorodiethyl ether; however, the protonated ether spontaneously split into HF , CF_4 , and other fragments, preventing an accurate determination of the proton affinity. Theoretical determinations of the proton affinity of fluorinated ethers will be reported shortly.³²

Neat cocondensation of BF_3 with $(\text{C}_2\text{F}_5)_2\text{O}$ failed to yield any new absorptions; the infrared spectrum was simply the sum of the two neat components. If there were new absorptions that were just too weak to detect, we would expect that they would be nonetheless shifted from those of the parent molecules. In annealing studies of the neat codeposited sample, new absorptions were detected when the temperature of the sample reached about 105 K . This was the only system where annealing was necessary to observe any interaction between the reactant molecules. The new absorptions that did appear upon annealing were reproducible, appearing at the same

frequency and relative intensities in several different neat samples, and showing appropriate shifts from the vibrational frequencies of the pure components. However, the sample was beginning to sublime at these temperatures, and indeed was lost at about 110 K. Therefore, one must question whether these new absorptions are indicative of interactions between the molecules or are due to structural changes in the solid as it sublimes. Regardless, the positions and relative intensities were the same for the several neat samples studied; the frequencies of the new absorptions are listed in Table IV.

The trend indicated by the relative reactivities of the various substituted ethers towards BF_3 is clear: the more the number of fluorine atoms on the ether, the less the obvious base character the ether exhibits towards the strong Lewis acid.

Application to lubricant systems As stated earlier, the catalytic degradation of commercial fluoroether lubricants by metal halides and metal oxides is of continuing interest to tribologists and engineers in the development of advanced lubrication systems. With very few exceptions, the proposed catalysis mechanisms invoke acidic attack of the ether's oxygen lone-pair electrons by surface acid sites. Despite the nearly universal acceptance of this scheme, however, the in-situ observation of an acid-base complex involving a fluoroether has not been reported to date. Indeed, a serious attempt was made in this laboratory to observe protonation of several perfluoroalkyl ethers by magic acid (HF/SbF_5) at -78°C , but no ^1H NMR signal could be detected for the protonation, suggesting a greatly lowered basicity for the oxygen atoms in these molecules compared to hydrocarbon ethers. The results reported in this study confirm the greatly lowered reactivity of highly fluorinated ethers towards Lewis acid complexation. They suggest that initiation of the catalyzed degradation by Lewis acids involves a more complicated process than mere electron transfer from ether oxygen to surface sites. Mechanisms involving nucleophilic attack at the carbon atom has been suggested by Yates et al.¹⁵ for adsorption of partially fluorinated ethers on Al_2O_3 . Our results suggest that this process at least contributes to the breakdown of the commercial products, especially in view of the highly polar C-O bonds.³⁻⁵

The perfluoroethers' reactivity towards nucleophilic reagents have not been explicitly studied to date. These results suggest that this would be a fruitful area to focus further attention. In addition, effort should be focussed on attempting to measure the spectral characteristics of the perfluoroether molecules adsorbed on a metal oxide or metal halide surface.

Our experiments indicate that classic complex formation between the Lewis acid BF_3 and fluoroether's oxygen atoms does not occur. This suggests that decomposition of poly(perfluoroether) lubricants by metal oxide surfaces is necessarily assisted by some other process.

Acknowledgments

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Table I. Infrared Absorptions (cm^{-1}) of $\text{BF}_3\text{—H}_2\text{O}$ and $\text{BF}_3\text{—D}_2\text{O}$ in Argon Matrices

$\text{BF}_3\text{—H}_2\text{O}$	$\text{BF}_3\text{—D}_2\text{O}$	Approximate assignment
3730.0	2721.3	asym O-H str
3555.1	2684.0 2629.7	sym O-H str
1314.6	1305.1	asym B-F str
1283.9	1292.8	
1264.7	1274.8	
1251.9	1259.4 1247.6	
874.5	870.6	sym B-F str
851.5	851.6	
691.5	690.9	BF_3 out-of-plane wag
664.0	664.5	BF_3 out-of-plane wag
654.9	—	H_2O libration/wag

Table II. Infrared Absorptions of the $\text{BF}_3\text{—}(\text{C}_2\text{H}_5)_2\text{O}$ Complex In Ar Matrices

Frequency	Approximate assignment
1241.1	antisym B-F str
1207.6	antisym B-F str
875.8	sym C-O str
796.8	sym ^{10}B -F str
762.0	sym ^{11}B -F str

Table III. Infrared Absorptions of the $\text{BF}_3\text{—}(\text{CF}_3\text{CH}_2)_2\text{O}$ Complex In Ar Matrices

Frequency	Approximate assignment
1330.0	perturb. of $(\text{CF}_3\text{CH}_2)_2\text{O}$
1229.6	perturb. of $(\text{CF}_3\text{CH}_2)_2\text{O}$
1220.0	perturb. of $(\text{CF}_3\text{CH}_2)_2\text{O}$
1116.1	perturb. of $(\text{CF}_3\text{CH}_2)_2\text{O}$
694.9	perturb. of ν_2 , $^{10}\text{BF}_3$
668.0	perturb. of ν_2 , $^{10}\text{BF}_3$

Table IV. New Infrared Absorptions Appearing Upon Annealing of $\text{BF}_3 + (\text{C}_2\text{F}_5)_2\text{O}$ to 105 K

1313 wk
1303 wk
1298 wk
1189 s
1170 s
1094 s

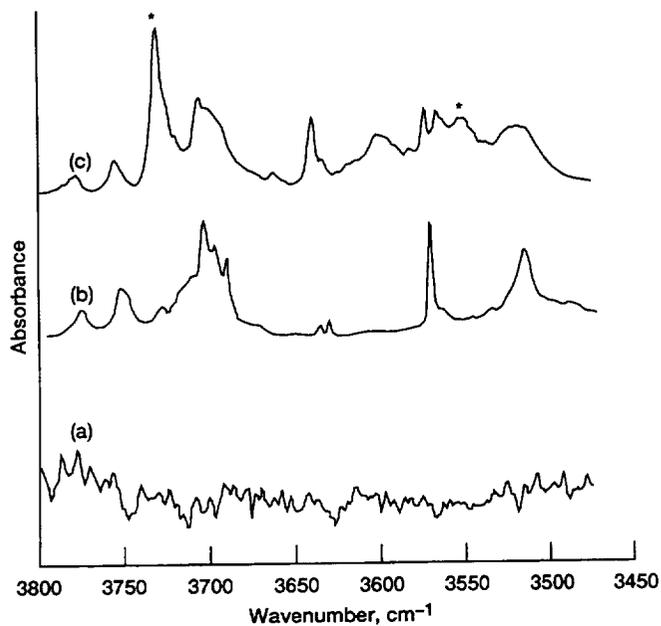


Figure 1.—Portions for the infrared spectra of BF_3 and H_2O in excess argon at 15K. New absorptions in (C), marked with an *, indicate the formation of the $\text{BF}_3\text{—H}_2\text{O}$ complex. (a) $\text{BF}_3\text{:Ar} = 3\text{:}1000$. (b) $\text{H}_2\text{O:Ar} = 5\text{:}1000$. (c) $\text{BF}_3\text{:H}_2\text{O:Ar} = 3\text{:}5\text{:}1000$.

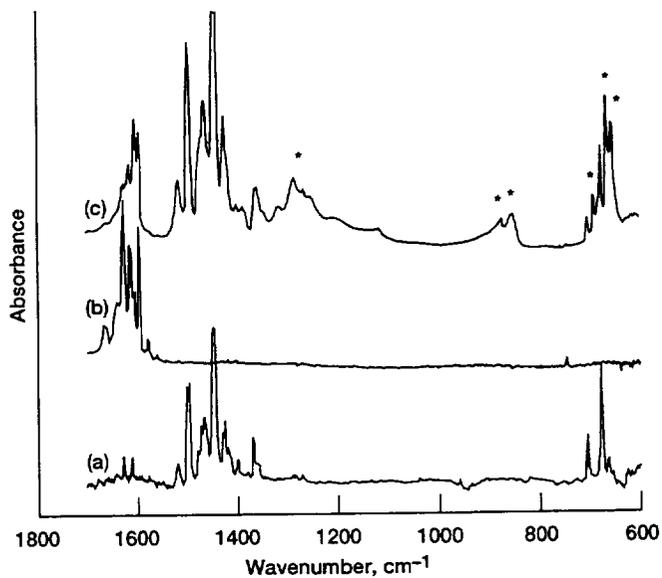


Figure 2.—Same as Figure 1, lower IR energy range. New absorptions are marked with an *.

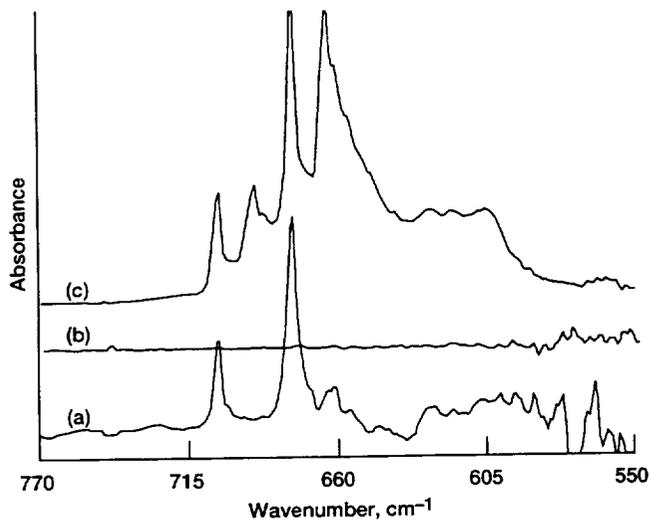


Figure 3.—A magnified view of the infrared spectrum where the ν_2 out-of-plane vibrational mode for BF_3 absorbs, showing the perturbational character of the new absorptions of the $\text{BF}_3\text{—H}_2\text{O}$ complex. Cf. Figure 2. (a) $\text{BF}_3\text{:Ar} = 3\text{:}1000$. (b) $\text{D}_2\text{O:Ar} = 10\text{:}1000$. (c) $\text{BF}_3\text{:D}_2\text{O:Ar} = 3\text{:}10\text{:}1000$.

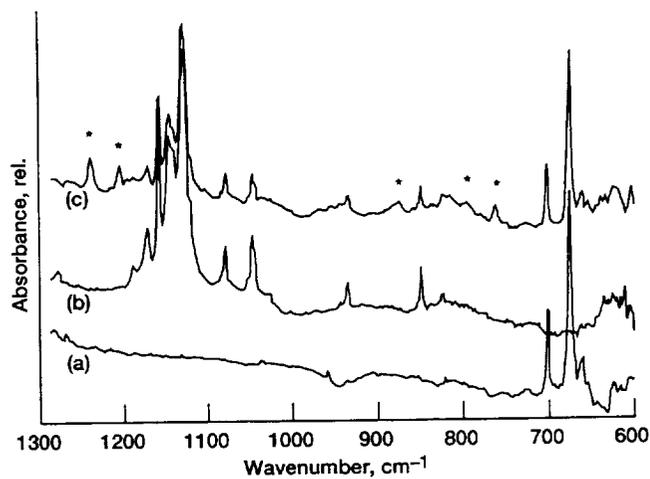


Figure 4.—Infrared spectra of BF_3 and diethyl ether in excess argon at 15K. New absorptions are marked with an *. (a) $\text{BF}_3\text{:Ar} = 3\text{:}1000$. (b) $(\text{C}_2\text{H}_5)_2\text{O:Ar} = 8\text{:}1000$. (c) $\text{BF}_3\text{:}(\text{C}_2\text{H}_5)_2\text{O:Ar} = 4\text{:}7\text{:}1000$.

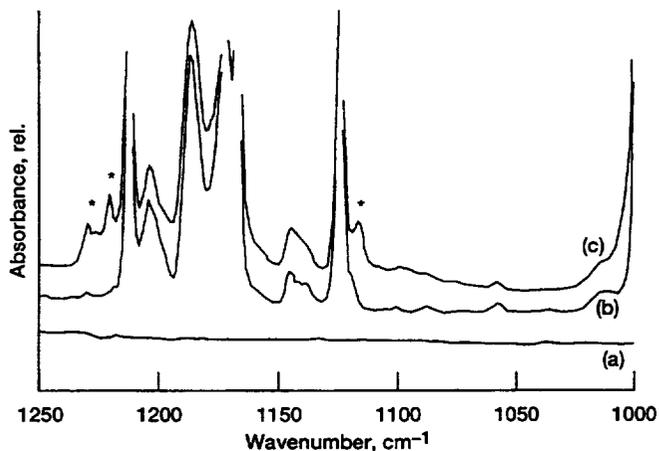


Figure 5.—Infrared spectra of BF_3 and bis(2,2,2-trifluoroethyl) ether in excess argon at 15K. New absorptions are marked with an *. (a) $\text{BF}_3:\text{Ar} = 3:1000$. (b) $(\text{CF}_3\text{CH}_2)_2\text{O}:\text{Ar} = 2:1000$. (c) $\text{BF}_3:(\text{CF}_3\text{CH}_2)_2\text{O}:\text{Ar} = 3:2:1000$.

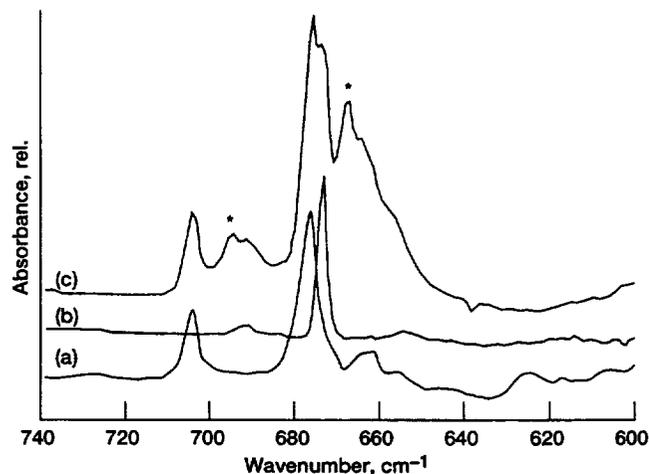


Figure 6.—Infrared spectra showing the perturbation of the BF_3 modes by $(\text{CF}_3\text{CH}_2)_2\text{O}$ in excess Ar at 15K. Sample concentrations are same as in Figure 5. Note that the new absorptions marked with * are separated by almost the same amount as the unperturbed $^{10,11}\text{BF}_3$.

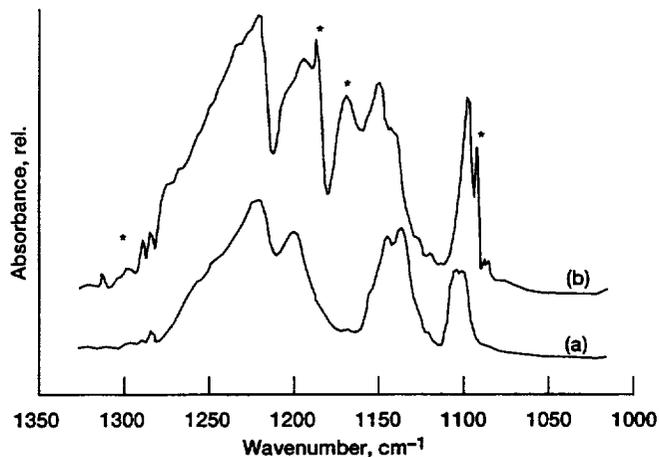


Figure 7.—Infrared spectra of neat BF_3 and perfluoroethyl ether. (a) Spectrum taken at 15K. (b) Spectrum taken at 15K after annealing the sample to $\sim 105\text{K}$. New absorptions are marked with an *.

REPORT DOCUMENTATION PAGE

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