Surface Chemistry of Perfluoroether: A Study of the Reaction Mechanism of $(C_2F_5)_2O$ with an Al₂O₃ Surface by FTIR Spectroscopy

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The decomposition of perfluorodiethyl ether on alumina has been studied at 300 and 500 K by transmission infrared spectroscopy using excess ether under high-pressure conditions. It was found in this study that the reaction products include trifluoro-, difluoro-, and monofluoroacetate, fluoroformate, alkyl acetate, and alkyl formate. The initial formation of trifluoroacetate probably results from a nucleophilic attack at the α -carbon of the ether by a surface oxygen anion. Subsequently, fluorine atoms, abstracted by coordinately unsaturated (cus) aluminum atoms, are replaced by hydrogen atoms donated by isolated surface hydroxyls. There is also evidence that fluoroalkene and fluoroalkyne resulted from the decomposition of initial surface adsorbates.

Introduction

Perfluoro polyethers are promising candidates for use as lubricants in areas of extreme environmental stress such as aerospace engines and satellite instruments due to their high thermal stability, low vapor pressure, and small temperature dependency of viscosity.¹ The stability of the C-C, C-O, and C-F bonds, and the chemically inert C-O-C ether bond make these molecules more stable to thermal and oxidative breakdown than analogous hydrocarbons. Nevertheless, these lubricants do break down under thermal and oxidative conditions.²⁻⁵ Approaches to improving their performance include developing an antioxidant lubricant additive, adding a protective moiety onto the perfluoro polyether molecule, or adding a protective group to the surface. Which of these approaches is more efficient cannot be predicted because the reaction mechanism of the ether-surface interaction is not understood on a molecular scale.

One method of examining the degradation reaction of these lubricants on surfaces has been to combine the lubricant with an oxide in a reactor and to collect the resultant gases, which are then characterized using MS and NMR techniques.^{6,7} Additionally, thermal desorption studies have examined lubricants on metal and metal oxide surfaces.^{2,8-10} Reactions of small model ether molecules on oxide surfaces suggest that the failure of perfluoro ether lubricants involves the cleavage of the ether and the formation of surface adsorbates.¹¹⁻¹³ The most productive way to elucidate the mechanism of perfluoro ether reaction with a surface is to *observe the surface in situ*.

We have used transmission infrared spectroscopy to study the reaction of $(C_2F_5)_2O$ with an Al_2O_3 surface. This compound has been used previously to model the reaction of poly(perfluoro ethers) with oxide surfaces.^{14–17} The advantages of infrared analysis are as follows: (1) the reaction can be observed in situ at known temperatures and pressures; (2) the purity of each sample and the uniformity of all sample surfaces can be assured; (3) the spectrum of the reaction products allows us to identify adsorbates directly without resorting to other analytical techniques, i.e. AA, ICP, or GC, which necessitate the introduction of additional solvents; and (4) our data analysis technique allows us to distinguish between physisorbed and chemisorbed species and between subsequent desorption and decomposition products. We have elected to begin the study of perfluoro polyethers by modeling these compounds using a smaller, less complex molecule, $(C_2F_5)_2O$. Two advantages are apparent: unlike viscous poly(perfluoro ether), $(C_2F_5)_2O(g)$ can be dosed onto a surface through a gas-handling system in a controlled manner, and its infrared spectrum is less complex than that of a poly-(perfluoro ether).

We selected Al_2O_3 as the first oxide surface examined because it is well characterized, can be readily and reproducibly prepared, and provides a heterogeneous array of oxidative and coordinately unsaturated (cus) aluminum sites which react with electrondonor and electron-acceptor molecules.

In a prior experiment, perfluorodiethyl ether was frozen on an alumina surface at 100 K and heated to 600 K under vacuum.¹² Carboxylates, identified as fluorinated acetates and fluoroformate, were observed on the surface immediately following the vaporization of the ether at approximately 147 K. Physisorbed and weakly chemisorbed ether, which did not entirely desorb until the surface temperature was >400 K, was also present.

The carboxylate intensities continued to increase throughout the duration of the experiment as the ether was oxidized. We concluded that increasing carboxylate intensities were a function of increasing concentration of product. Conversely, the C-F stretching modes decreased as the temperature was heated to 600 K. This suggested several possibilities: (1) fluorinated carboxylates desorbed from the surface as temperature increased; (2) the fluorinated carboxylates subsequently decomposed or were transformed into other species; or (3) the decrease in intensity resulted from the change in orientation with respect to the surface.

The concentration of ether on the surface was limited under UHV conditions. As a result, the spectra did not show reaction products with low absorbance. It could not be determined whether the appearance of a product was a function of time or temperature. The present study was conducted with excess ether at constant temperature in order to maximize the concentration of reaction products and to equate product formation with temperature. There are several questions we hoped this study would answer. Can we deduce whether the surface oxygen forming the carboxylate is derived from hydroxyl or anionic oxygen? Can we observe additional reaction products? Is the reaction mechanism the same at 300 and 500 K? Are active sites recycled as the reaction progresses? Can we propose a

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mechanism which explains our results as well as those of other researchers who have suggested alternative pathways?

Experimental Section

The infrared spectra were measured using a purged ATI Mattson Galaxy 2020 FTIR spectrophotometer with the First data analysis package. Resolution was 2.0 cm^{-1} with an acquisition time of 14 s for five scans from 4000 to 1000 cm⁻¹. Experimentation with an increased number of scans and data acquisition time did not result in a better signal-to-noise ratio.

The sample chamber was purged by CO_2 -free dry air from a Balston air dryer. Due to the long reaction times, the minor rotational structure of atmospheric water was evident in the spectra. These features were removed by subtraction prior to any other data manipulation. Thirteen-point boxcar smoothing was applied in the region from 4000 to 3000 cm⁻¹ in all spectra. Smoothing was also applied to the region from 1800 to 1400 cm⁻¹ as needed. Other regions of the spectra were unsmoothed.

Sample preparation has been described previously.¹² Briefly, a slurry of approximately 1 g of Degussa Aluminum Oxide C in a 1:8 water/acetone mixture was sprayed onto half of a one inch diameter calcium fluoride disk. The disk was heated by a heat lamp during spraying to flash evaporate the acetone. The samples for the 300 and 500 K experiments weighed 24.4 and 28.1 mg, respectively.

The sample was mounted in a UHV stainless steel cell which has been previously described.¹⁸ The main cell body contains a copper/stainless steel ring which supports the CaF₂ disk. The temperature of the sample was maintained at 500 K by passing heated air through the support ring. A chromel-alumel thermocouple attached to the ring was used to monitor the sample temperature. The cell body is contained between two CaF₂ optical windows sealed in stainless steel flanges, permitting IR measurements in the 4000-1000 cm⁻¹ range. The IR cell is attached to a grease-free stainless steel gas-handling system and is maintained at a base pressure of $P \le 1 \times 10^{-7}$ Torr by a Leybold TMP50 turbo pump backed by a D 1.5 Vane pump. Before the experiments the samples were heated at 475-500 K for 24 h in vacuo.

In the 500 K experiment, the sample was equilibrated at temperature for approximately 1 h prior to $(C_2F_5)_2O$ exposure. The initial $(C_2F_5)_2O$ pressures were 2.431 and 2.707 Torr, respectively, at 300 and 500 K. Equilibrium conditions were reached following 8.0 h of reaction time at 500 K and ~20.0 h of reaction time at 300 K.

During the experiments, the cell was translated in the IR beam path in order to acquire spectra on both the alumina surface and the blank CaF_2 disk. The contribution from the gas phase can thereby be determined. The difference spectra presented here were obtained by a three-step subtraction procedure: (1) Before exposure to dosing of $(C_2F_5)_2O$, spectra were acquired on each half of the CaF_2 disk. These spectra were subtracted to yield a spectrum of the clean alumina surface.

$$(Al_2O_3 + CaF_2)_{clean} - (CaF_2)_{clean} = (Al_2O_3)_{clean}$$

(2) Spectra of adsorbates on alumina were obtained by subtracting the CaF_2 spectrum acquired at each time from the alumina spectrum acquired at the same time.

$$(adsorbate + Al_2O_3 + CaF_2)_t - (CaF_2)_t =$$

 $(adsorbate + Al_2O_3)_t$

(3) The clean alumina spectrum was subtracted from each spectrum of adsorbates on alumina. These spectra of the thermal



Figure 1. Change in cell pressure with time during reaction of $(C_2F_5)_2O$ with Al_2O_3 : top, 500 K; bottom, 300 K.

behavior of the adsorbates are presented here.

$$(adsorbate + Al_2O_3)_t - (Al_2O_3)_{clean} = (adsorbate)_t$$

Spectral deconvolution was accomplished using the Curvefit program in the Spectra Calc software by Galactic Industries Corporation. Briefly, parameters defining height, frequency, and width at half maximum were entered for each peak defined. 100% Gaussian character was selected. The χ^2 values for the fitted curves were less than 0.000 05.

Thirteen peaks were fitted over a 400 cm^{-1} range from 1800 to 1400 cm⁻¹. The peaks fitted were selected because (1) they were evident in the acquired spectra or (2) they were observable as underlying peaks at locations where a change in the slope of the initial acquired spectra was apparent and subsequent subtraction between spectra acquired at different times revealed the presence of the peaks.

The reagent used in this study, $(C_2F_5)_2O$ (90% minimum purity, certified to be completely fluorinated with no H, OH, or acid groups present, Strem), was transferred to a glass storage flask and purified by several freeze-pump-thaw cycles with liquid nitrogen. The gas phase IR spectrum of the transferred $(C_2F_5)_2O$ did not show any peaks in the OH or COO⁻ stretching region. The mass spectrum of the gas phase ether shows no 14, 18, or 44 amu peaks. Other researchers also found that the very small amount of "impurity" is a fluorine-containing chemical similar to $(C_2F_5)_2O$.¹⁹ Acetone used was spectral grade, 99.7% purity, J. T. Baker. Water was treated by a Nanopure filter system.

Results

Changes in Pressure in System during Reaction. During each experiment 4.000 Torr of $(C_2F_5)_2O$ was expanded into a section of the gas-handling system. The pressure dropped as the ether was expanded into the cell containing the sample. The initial pressures measured 2.431 and 2.707 Torr at 300 and 500 K, respectively.

The changes in pressure with respect to time are shown in Figure 1. Desorption of reaction products from the surface occurred from the onset of the reaction at 500 K. Pressure increased at a rate of 0.283 mTorr/min until an equilibrium level of 2.86 Torr was reached after 8.0 h. For the reaction at 300 K, the pressure decreased asymptotically, reaching an equilibrium level of 2.3 Torr after 20.0 h. The decrease in pressure results from hydrogen bonding of the ether to the surface, as



Figure 2. Infrared spectra of hydroxyl groups of Al_2O_3 after 8 h of reaction with $(C_2F_5)_2O$: a, 300 K; b, 500 K.

shown in our previous work, and the formation of products which do not desorb from the surface.

Reaction of $(C_2F_5)_2O$ with Hydroxyl Groups on the Al₂O₃ Surface. Isolated and associated hydroxyls are produced during the heating pretreatment of the alumina surface. The presence of these hydroxyls is a function of the temperature at which the sample is heated. The heat pretreatment of our samples yielded alumina surfaces with isolated hydroxyls absorbing at 3780, 3723, and 3676 cm⁻¹ and associated hydroxyl absorbing at ~3588 cm⁻¹.

Infrared difference spectra of surface species resulting from the reaction of $(C_2F_5)_2O$ with the Al₂O₃ surface at 300 and 500 K are shown in Figure 2. Spectra acquired after 8.0 h of reaction time are used to compare the effect of temperature on the reaction rates at the two temperatures. Negative going absorption features in Figure 2 indicate depletion of band intensities, and positive features are due to the development of new or existing bands. Negative bands are present at 3775, 3745, and 3694 cm⁻¹. The depletion of these hydroxyl features at 300 K is approximately half of that observed at 500 K. Associated hydroxyl increases over time, forming a broad bnad from ~3700 to 3300 cm⁻¹ at both temperatures.

The spectra acquired after 0.08, 0.50, 1.5, 3.0, and 10.0 h of reaction time at 500 K are shown in Figure 3. The intensity of the peak at 3745 cm⁻¹ decreases 2.3 fold between 0.08 and 10.0 h. The 3780 cm⁻¹ vibrational mode shifts to \sim 3770 cm⁻¹, finally appearing as a shoulder. The 3694 cm⁻¹ feature is not a depletion band because it remains constant over time. It appears to be a negative-going absorption feature because the baseline in this portion of the spectrum is affected by areas of increasing intensity at higher and lower frequencies. The apparent increase in intensity at 3714 cm⁻¹ may result from (1) a decrease in the frequencies of ν (OH) of the hydroxyls at 3780 and 3745 cm⁻¹, (2) the presence of a new and distinct isolated hydroxyl at this frequency, or (3) the higher frequency tail of the broad band of associated hydroxyls.

Reaction of $(C_2F_5)_2O$ with the Al₂O₃ Surface in the Carboxylate Region. Figure 4 shows the infrared absorption spectra of surface species in the carboxylate region after 0.08,



Figure 3. Four overlaid IR spectra of hydroxyl groups of Al_2O_3 following reaction with $(C_2F_5)_2O$ at 500 K. Reaction times, from least negative to most negative 3745 cm⁻¹ intensity, correspond to 0.08, 1.5, 3.0, and 10.0 h.



Figure 4. Infrared spectra in the region $1900-1300 \text{ cm}^{-1}$ showing characteristic vibrational modes of carboxylates on Al₂O₃ at 300 K: a-e, 0.08, 1.5, 3.0, 8.0, and 32.0 h.

1.5, 3.0, 8.0, and 32 h of reaction at 300 K. Vibrational features at 1750, 1645 (sh), 1615, \sim 1470, and 1375 cm⁻¹ are observed. Changes in the profiles of the features are apparent when segments of the spectra are enlarged. These changes are seen at 1590 cm⁻¹ (1.5 h), 1675 cm⁻¹ (3.0 h), 1700 and 1570 cm⁻¹ (8.0 h), and 1525 cm⁻¹ (32 h). This indicates that the envelope contains more underlying peaks which are not readily distinguishable.

In addition to the features observed at 300 K, the 500 K spectra in Figure 5 show features at 1700, 1575 (sh), ~1475, and ~1440 cm⁻¹. Comparison of the initial spectra at 5 min in Figures 4a and 5a shows that the bands at ~1615 and 1645 cm⁻¹ have higher intensity at 500 K. The relative changes in intensity of the bands at ~1645 (sh), 1615, and 1440 cm⁻¹ suggest that they are ν (O-C-O) stretching modes of adsorbed



1900 1800 1700 1600 1500 1400 1300 Wavenumbers (cm⁻¹)

Figure 5. Infrared spectra in the region $1900-1300 \text{ cm}^{-1}$ showing characteristic vibrational modes of carboxylates on Al₂O₃ at 500 K: a-e, .08, 1.5, 3.0, 8.0, and 10.0 h.

carboxylate. The difference spectrum, not shown, obtained by subtracting spectrum 5a from 5b reveals that there are at least two $v_s(OCO)$ modes at 1447 and 1472 cm⁻¹. The $v_s(OCO)$ mode at 1447 cm⁻¹ is associated with the $v_{as}(OCO)$ modes at 1648 cm⁻¹. The $v_s(OCO)$ mode at 1472 cm⁻¹ is associated with the $v_{as}(OCO)$ mode at 1575 cm⁻¹. After 1.5 h the 1700 cm⁻¹ feature appears as a shoulder and increases in intensity as the reaction progresses. Similarly, the shoulder at ~1465 cm⁻¹ increases in intensity and shifts to 1475 cm⁻¹ after 10.0 h. The appearance of a feature may be a function of more favorable reaction conditions at a given temperature or the absence of a nearby overlapping feature. The production of the species at 1700 cm⁻¹ is favored at 500 K. Similarly, the decrease in intensity and sharpening of the feature at ~1600 cm⁻¹ permits the observation of a shoulder at 1575 cm⁻¹.

Reaction of $(C_2F_5)_2O$ **with Al₂O₃ from 1200 to 1000 cm⁻¹.** Figure 6 shows spectra acquired after 0.08, 1.5, 3.0, 8.0, and 32.0 h of reaction at 300 K. Initially, vibrational modes are observed at 1241, 1215 (sh), 1149, and 1106 cm⁻¹. As the reaction progresses, a shoulder at 1271 cm⁻¹ appears after 1.5 h. The 1241 cm⁻¹ vibration shifts to 1234 cm⁻¹. The shift in frequency is due to the increase in intensity and broadening of the 1214 cm⁻¹ feature. The 1214 cm⁻¹ feature continues to increase in intensity and is the most prominent feature in the spectrum after 3.0 h. The vibration at 1149 cm⁻¹ is shifted to 1155 cm⁻¹ as a new feature develops and is observed as a shoulder at ~1169 cm⁻¹. The absorbance at 1106 cm⁻¹ increases steadily over time.

This region of the spectra is difficult to interpret due to the complexity of the IR bands. $(C_2F_5)_2O$ is a molecule that contains atoms with similar masses (C, 12; O, 16; F, 19) and bonds with similar force constants (k_e values for C-F, C-O, and C-C are 5.9 \times 10², 4.89 \times 10², 4.5 \times 10² N/m, respectively). It is not possible to find vibrations which are independent and characteristic for each bond, nor can we distinguish pure bond-stretching or pure bond-bending vibrations.

In Figure 7, the spectra acquired after 0.08, 0.5, 1.5, 3.0, and 10.0 h at 500 K are shown. The frequency of the vibrational modes can be determined more accurately due to the desorption and/or decomposition of some of the surface adsorbates and



Figure 6. Infrared spectra in the region $1300-1000 \text{ cm}^{-1}$ showing $\nu(C-F)$ and $\nu(C-O)$ modes of adsorbed species following $(C_2F_5)_2O$ reaction with Al₂O₃ at 300 K: a-e, 0.08, 1.5, 3.0, 8.0, and 32.0 h.



Figure 7. Infrared spectra in the region $1300-1000 \text{ cm}^{-1}$ showing $\nu(C-F)$ and $\nu(C-O)$ modes of adsorbed species following $(C_2F_5)_2O$ reaction with Al₂O₃ at 500 K: a-e, 0.08, 1.5, 3.0, 8.0, and 10.0 h.

the absence of physisorbed perfluorodiethyl ether at the higher temperature. The 0.08 h spectrum in Figure 7a shows a peak at 1208 cm⁻¹, which increases with time. At 0.5 h vibrational modes are observed at 1268, ~1250, 1150 (sh), and 1119 cm⁻¹. At 1.5 h the 1244 cm⁻¹ band is observable and another underlying peak appears at ~1175 cm⁻¹. Between 3.0 and 10.0 h, the 1179 cm⁻¹ mode increases in intensity relative to the 1159 cm⁻¹ mode.

Other researchers have made assignments for some of these vibrational features using partially fluorinated ethers. These assignments have been discussed previously.¹² Our initial experiment was conducted under UHV conditions with limiting amounts of ether. As the sample surface was heated from 100 to 600 K, the intensities of ν (OCO) modes increased whereas the intensities of ν (CCO) modes decreased. The use of excess ether in the present experiment has resulted in spectra with more intense and better resolved peaks in the 1200–1000 cm⁻¹ range.



Figure 8. Integrated intensity of 2258 cm⁻¹ feature on Al₂O₃ following reaction with $(C_2F_5)_2O$. Top scale shows intensities at 500 K measured over 10.0 h. Bottom scale shows intensities at 300 K measured over 32.0 h.

We now assigned the features as follows: $\nu(CF_3)$ at 1268 cm⁻¹, $\nu(CF_2)$ at 1244 cm⁻¹, $\nu(CF)$ at 1209 cm⁻¹, unidentified combination modes at ~1180-1150 cm⁻¹, and $\nu(CF_3+CF_2)$ at ~1119 cm⁻¹. These assignments are made by examining spectra of diethyl ether, tetrafluorodimethyl ether, perfluorodiethoxymethane, and Fomblin Z adsorbed on alumina and perfluorodiethyl ether adsorbed on aluminum trifluoride. In addition, ab initio SCF calculations of the vibrational frequency of gaseous perfluorodiethyl ether published by Pacansky et al. are related to our experimental values by the equation Y =-393.7 + 1.327X with a correlation coefficient of 0.9976.¹⁹

Intensity of the Vibrational Feature at 2258 cm⁻¹. The integrated intensity of a vibrational feature observed at 2258 cm⁻¹ in the 500 and 300 K spectra is shown in Figure 8. At 500 K the intensity rapidly increased during the first two hours of the experiment and then decreased at a slower rate until reaching an equilibrium level after 8.0 h of reaction time. The absorbance of this mode at equilibrium was approximately 1/15 of the absorbance of the feature at 1615 cm⁻¹. At 300 K, this vibrational mode was barely discernible above noise level during the first 1.5 h of the experiment. After 1.5 h of reaction time the intensity slowly increased until reaching equilibrium at 20.0 h. Comparison of the integrated intensities at equilibrium, 10.0 h at 500 K and 32.0 h at 300 K, shows that this feature is ~40% smaller at 300 K.

Discussion

Deconvolution and Assignment of Carboxylate Peaks. It is obvious that the absorption band centered around 1610 cm^{-1} in Figures 4 and 5 consists of overlapping vibrational modes. In an attempt to identify these modes, a deconvolution of the band between 1800 and 1400 cm⁻¹ was performed. The Curvefit program in the SpectraCalc software distributed by Galactic Industries Corporation was used to perform the deconvolution on *all* the spectra at *both* temperatures. The thirteen curves identified meet the following criteria: they represent (1) features where bands were observed initially or (2) features where a change in the slope of the spectra indicated overlapping absorbance features, and subsequent subtraction between spectra acquired at different times revealed the presence



Figure 9. Deconvolution of the IR spectrum of Al_2O_3 acquired at 500 K following 10 h of reaction with $(C_2F_5)_2O$. Peaks are identified at a, 1756; b, 1726; c, 1700; d, 1675; e, 1637; f, 1615; g, 1595; h, 1575; i, 1552; j, 1515; k, 1496; l, 1475; and m, 1449 cm⁻¹. Dotted line is cumulative spectrum.

of these peaks. Because so many curves were fitted to each spectrum, it was not possible to use a mixture of Gaussian/ Lorentzian character. The wide tails of many overlapping Lorentzian curves would distort the baseline such that a fit could not be made. The curve-fitting example presented in Figure 9 is that of the equilibrium spectrum acquired after 10.0 h at 500 K. Curves a-m have the following frequencies: 1756, 1726, 1700, 1675, 1637, 1615, 1595, 1575, 1552, 1515, 1496, 1475, and 1449 cm⁻¹. All of the 300 K spectra exhibit an additional weak, broad absorbance at ~1770 cm⁻¹. Otherwise, at 300 K, the same features were present.

The frequencies of the $\nu_{as}(OCO)$ of fluorinated carboxylate ions range from 1695 to 1615 cm⁻¹.²⁰ The frequency of the asymmetric carboxylate stretching mode increases with the electron-withdrawing effects of substituents. Each additional fluorine increases $\nu_{as}(OCO)$ by approximately 30 cm⁻¹.²¹ Cleavage of the (C₂F₅)₂O between the α -carbon and oxygen would leave one C-C and one C-C-O fragment available for reaction with the alumina surface. Consequently, we expect that oxidation by the surface to form carboxylates should be limited to the production of formate and acetate species.

Our assignment of the carboxylate absorption features is based on the following criteria: (1) the IR absorption spectra of gas phase and adsorbed surface species of $(C_2F_5)_2O$ and $(HF_2C)_2O$ obtained in our laboratory; (2) assignments of gas phase $(C_2F_5)_2O$ absorption features in ref 19; (3) comparison with published IR spectra of fluorinated carboxylic acids and salts;^{15,19,21-29} and (4) simulation of vibrational modes of $(C_2F_5)_2O$, CF₃COOAI, and FCOOAI using HyperChem software. The theoretical IR spectra were computed by semiempirical calculations using a PM3 parameter set. PM3 is based on the NDDO approximation with the parameters being derived from comparison of a large number and wide variety of experimental versus computed molecular properties. We assign the absorption features as $\nu_{as}(OCO)$ modes of the following adsorbed species: 1700 cm⁻¹, trifluoroacetate; 1675 cm⁻¹ difluoroacetate; 1637 cm⁻¹, monofluoroacetate, 1615 cm⁻¹, fluoroformate; 1595 cm⁻¹, alkyl formate; and 1575 cm⁻¹, alkyl acetate.

The absorbances at 1495, 1475, and 1440 cm⁻¹ are identified as $v_s(OCO)$ modes. The range of the $v_s(OCO)$ is narrower than that of the $v_{as}(OCO)$ because the frequencies of these modes are not as significantly affected by fluirination. Spectra of fluorinated sodium acetates published by Spinner showed that $v_{as}(OCO)$ frequencies were 1446, 1448, and 1421 cm⁻¹ for trifluoroacetate, monofluoroacetate, and alkyl acetate.²¹ Greenler's spectrum of aluminum acetate identifies the $v_s(OCO)$ mode at 1466 cm^{-1,26} This represents a shift of 45 cm⁻¹ with respect to Spinner's values. By analogy, a similar shift in the frequency of $v_s(OCO)$ of trifluoro- and monofluoroacetate results in peaks at 1491 and 1493 cm⁻¹.

The heights of the deconvoluted $\nu_{as}(OCO)$ modes of the carboxylates range from ~0.12 to 0.05 absorbance units. The ratio of the relative heights of the absorbances of the $\nu_{as}(OCO)$: $\nu_s(OCO)$ frequencies in Figure 9 is ~3:1. The noise level of the spectra is approximately 0.003 units; consequently, the individual $\nu_s(OCO)$ frequencies of all six carboxylates cannot be distinguished. Similarly, the ratio of $\nu_{as}(OCO):\delta(CH_3):\nu_{as}-(CH)$ of trifluoroacetate and alkyl acetate is ~70:10:1.²¹ The intensities of characteristic C–H vibrational modes of the partially fluorinated carboxylates are not observable above noise level.

The features at 1552 and 1516 cm⁻¹ have not been conclusively assigned. Greenler commented on an unexplained shoulder observed in a spectrum of aluminum acetate at 1549 cm^{-1,26} The 1516 cm⁻¹ feature could be a combination band due to the ν (Al–F) and ν (Al–O) modes at ~880 and 645 cm^{-1,30}

Assignment of Alkenyl and Alkynl Species. The most likely assignment for the feature at 2258 cm⁻¹ is the ν (C=C) of an adsorbed fluoroalkyne, (-C=CF)_{ads}. The ν (C=C) of HC=CF at 2255 cm⁻¹ was assigned by Hunt and Wilson.³¹ If fluoroalkyne is produced on the surface from fluoroethers, then a likely intermediate is fluoroalkene. The characteristic frequency of the ν (C=C) mode of a vinyl group, ($-CH=CH_2$), is ~1640 cm⁻¹. This frequency shifts to 1740 cm⁻¹ when the terminal hydrogen atoms are replaced by fluorine atoms. Substitution of the third hydrogen increases the frequency another 50 cm⁻¹ to 1790 cm^{-1,32,33} Brice et al. reported C=C vibrational frequencies for various fluorinated C₄ olefins at 1795, 1755, and 1735 cm^{-1,34} CF₂CH₂(g) has a fundamental C=C vibrational mode at 1728 cm⁻¹ and a very strong shoulder at 1740 cm^{-1,35}

The integrated intensity of the 2258 cm⁻¹ peak at 300 K in Figure 8a is half the size of the same absorbance at 500 K. Additionally, the curve-fitted peaks produced in the 300 K spectra show an additional absorbance at ~1770 cm⁻¹. Since production of the adsorbed fluoroalkyne increases with temperature, it is likely that the concentration of fluoroalkene will be greater at 300 K than at 500 K. Therefore, the vibrational modes at ~1770 and 1724 cm⁻¹ are assigned to the $\nu_{as}(C=C)$ and $\nu_{s}(C=C)$ of $(-C_{2}F_{3})_{ads}$.

In our previous work under UHV conditions, a limited amount of $(C_2F_5)_2O$ was in contact with the surface as the temperature was increased from 100 to 600 K. The fluoroalkyne was not observed until the temperature reached approximately 400 K. When the sample was maintained at 600 K, the intensity of the 2258 cm⁻¹ absorbance continued to increase for several hours before reaching an equilibrium level. This suggests that the fluoroalkyne results from the decomposition of a surface adsorbate.



Figure 10. Integrated intensities of ν_{as} (OCO) of fluorinated carboxylates as a function of time; temperature equals 300 K: \Box , 1700 cm⁻¹, trifluoroacetate; +, 1670 cm⁻¹, difluoroacetate; \diamond , 1645 cm⁻¹, monofluoroacetate; Δ , 1615 cm⁻¹, fluoroformate.



Figure 11. Integrated intensities of ν_{as} (OCO) of fluorinated carboxylates as a function of time; temperature equals 500 K: \Box , 1700 cm⁻¹, trifluoroacetate; +, 1670 cm⁻¹, difluoroacetate; \diamond , 1645 cm⁻¹, monofluoroacetate; Δ , 1615 cm⁻¹, fluoroformate.

The production of $(-AI-O-C\equiv CF)$ from adsorbed trifluoroacetate would require the loss of one oxygen and two fluorine atoms. The unsaturation of nearby cus aluminum(s) is reduced by 2 in the process of trifluoroacetate formation. The density of cus aluminum sites per adsorbed molecule is greater when $(C_2F_5)_2O$ is present in limiting concentrations, favoring alkynyl bond formation. Consequently, we see more fluoroalkyne produced in our previous UHV experiment. We have assumed that more fluoroalkyne is produced at 500 K because of the favorable thermodynamic conditions at the higher temperature. The underlying cause of the decreased concentration of fluoroalkyne observed at 300 K may be that $(C_2F_5)_2O(g)$ adsorbed on the surface adjacent to surface fluorocarboxylates sterically hinder the further reaction of the carboxylates with nearby cus aluminum sites.

Comparison of Reaction Rates at 300 and 500 K. Figures 10 and 11 show the concentrations of the four fluorinated carboxylate species, trifluoro-, difluoro-, and monofluoroacetate and fluoroformate, with respect to time, as represented by the integrated intensities of their $v_{as}(OCO)$ modes. At 300 K, the initial rates of increase in concentration of trifluoro-, difluoro-, and monofluoroacetate and fluoroformate measured from 0.0833–

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2.5 h are 0.4175, 0.3624, 0.9052, and 1.055 units/h, respectively. At 500 K the initial rates, measured from 0.0833-1.5 h, are 0.5172, 0.3067, 1.202, and 0.9336 units/h.

The ratios of the initial rates of adsorption of each species at 300 and 500 K (i.e. $[r_{300K}]:[r_{500K}]$) are 0.81, 1.18, 0.75, and 1.13 for trifluoro-, difluoro-, and monofluoroacetate and fluoroformate, respectively. The ratios of the initial rates of trifluoro- and monofluoroacetate are approximately equal, whereas the ratios of the rates of difluoroacetate and fluoroformate are similarly related.

The initial rates of adsorption of alkyl acetate and alkyl formate are 0.5655 and 0.6183 units/h at 300 K and 0.7081 and 0.5619 units/h at 500 K. The ratios of the rates at 300 and 500 K are 0.80 for alkyl acetate and 1.1 for alkyl formate. Again, the ratio for alkyl acetate is approximately equal to those of trifluoro- and monofluoroacetate. Likewise, the ratio of the rates of the alkyl formate is equal to those of difluoroacetate and fluoroformate.

The fact that the ratios of the initial rates at the two temperatures are similar for some adsorbed species suggests that these species are produced by the same reaction mechanism having the same activation energy. Another way of illustrating this point is to compare the ratios of the initial rates of adsorption between species at the same temperature. For example, if the same reaction mechanism is followed as fluorocarboxylates are successively alkylated, then the ratios of initial rates of [monofluoroacetate]:[alkyl acetate] and [fluoroformate]:[alkyl formate] should be approximately equal at 300 and 500 K. The acetate ratios at 300 and 500 K are 0.62 and 0.59, whereas the formate ratios are 0.59 and 0.60. These ratios suggest that we are indeed observing successive alkylation of fluorinated carboxylates.

At 300 K (Figure 10) the concentration of trifluoroacetate reaches an equilibrium level after 3.0 h. Difluoroacetate concentration continues to increase, finally reaching an equilibrium level between 20.0 and 32.0 h. Fluoroformate concentration equilibrates at 8.0 h, whereas monofluoroacetate formation continues, although at a slower rate, until the trial was ended at 32.0 h. The final ratio of the concentration of trifluoro-, difluoro-, and monofluoroacetate and fluoroformate was \sim 1: 1.5:4:3.

At 500 K (Figure 11) trifluoro- and difluoroacetate concentrations reach an equilibrium level after 8.0 h. At 0.08 h a substantial amount of fluoroformate is adsorbed on the surface. The rate of production and the total amount of fluoroformate produced is probably greater than is indicated in Figure 11 because at this temperature the intensity of the adsorbed species is a function of the rate of formation and the rate of decomposition and/or desorption. Fluoroformate concentration increases over 3 h and then decreases slowly, reaching an equilibrium concentration after 8.0 h. Monofluoroacetate concentration increases steadily over time, finally reaching an equilibrium level at ~ 10.0 h. The final ratio of trifluoroacetate:difluoroacetate: monofluoroacetate:fluoroformate is 1:0.8:5:2.5.

In Figure 12, the integrated intensities of $\nu_{as}(OCO)$ of alkyl formate (1595 cm⁻¹) and alkyl acetate (1576 cm⁻¹) formed at 300 and 500 K are presented as a function of reaction time. The x-axis along the top, 0–35 h, applies to the 300 K data, whereas the x-axis along the bottom of the graph, 0–10 h, applies to the 500 K data. At 500 K both alkyl formate and alkyl acetate concentrations increase at the same rate over the duration of the experiment. Following 10 h of reaction time at 500 K, the integrated intensity of $\nu_{as}(OCO)$ of alkyl acetate is 60% that of alkyl formate. At 300 K, the alkyl acetate and alkyl formate concentrations reach an equilibrium level between



Figure 12. Integrated intensities of $\nu_{as}(OCO)$ of alkyl formate and alkyl acetate as a function of time. Bottom: scale is 0–10.0 h at 500 K; \diamondsuit , 1595 cm⁻¹, alkyl formate; \triangle , 1576 cm⁻¹, alkyl acetate. Top: scale is 0–32.0 h at 300 K; \Box , 1595 cm⁻¹, alkyl formate; +, 1576 cm⁻¹, alkyl acetate.

20 and 32 h. The alkyl acetate concentration at 32 h is \sim 75% that of alkyl formate.

At 500 K the temperaure is sufficient to cause the desorption and/or decomposition of fluoroformate and other species. Comparison of the final concentrations of alkyl acetate and alkyl formate at 300 and 500 K shows that at 500 K the concentration adsorbed on the surface is $1/_2$ as much as the concentration at 300 K. We estimate that the difference in the concentrations is approximately equal to the concentration of the alkyl acetate and alkyl formate which desorbs from or is decomposed on the surface at 500 K.

The concentrations of alkyl acetate and alkyl formate at 500 K in Figure 12 increase throughout the duration of the experiment. These concentrations increase because the rate of formation of alkyl acetate and alkyl formate is greater than the rate of desorption and/or decomposition. In Figure 11 the kinetic plot of fluoroformate concentration shows a decrease because the rate of desorption and or decomposition is greater than the rate of formation after 3 h. This suggests that, as the active sites on the surface become limiting, existing surface adsorbates are preferentially alkylated. The rate of formation of new surface adsorbates is decreased due to steric hindrance by existing adsorbates or the depletion of oxide anions, isolated hydroxyls, and/or cus aluminum atoms at active sites.

Role of Hydroxyl in the Reaction of $(C_2F_5)_2O$ on Alumina. Peri identified five isolated hydroxyls ranging from most basic to most acidic at 3800, 3780, 3744, 3733, and 3700 $cm^{-1.36}$ The different $\nu(OH)$ frequencies are attributed to differing numbers of adjacent surface oxide sites. From highest to lowest frequency the number of surrounding oxides ranges from four to zero. The most reactive isolated hydroxyls observed at 3745 and 3780 cm⁻¹ have three and four oxide neighbors according to the Peri model, whereas the 3694 cm⁻¹ species, which showed no change in intensity during the experiment, has no adjacent oxide atoms. Knozinger and Ratnasamy modified Peri's assumption that the (100) face is dominantly exposed on α -Al₂O₃ surfaces and asserted that the projection of all low-index crystal faces is equally likely to occur.³⁷ The later model assigns the ν (OH) frequencies of the five isolated hydroxyls on the basis of the degree of coordination to octahedral and tetrahedral Al³⁺ sites.

Isolated hydroxyl groups perform several roles in the oxidation of $(C_2F_5)_2O$ by the Al_2O_3 surface and the subsequent reduction of the fluorinated carboxylates. Hydrogen bonding of the ether to surface hydroxyls may serve to position the ether at a reactive site. In Figures 2 and 3 we observe that associated hydroxyls are produced as isolated hydroxyls are depleted. This suggests that isolated hydroxyls interact with either the gaseous ether or the adsorbed reaction products.

The depletion of isolated hydroxyls may also result from a nucleophilic attack by an oxygen atom of an isolated hydroxyl on the α -carbon of F₃C-F₂C-O, forming adsorbed trifluoro-acetate. Although it is possible that adsorbed carboxylate is formed from the oxygen atoms of surface hydroxyls, the surface oxide is the most probable site of attachment for the α -carbon of the ether because (1) it is a site with high electron density, (2) the majority of isolated hydroxyl depletion occurs at those hydroxyls adjacent to oxide sites, and (3) no depletion of the isolated hydroxyl at 3694 cm⁻¹, with no adjacent surface oxide sites, is observed.

Mechanism of Reaction of $(C_2F_5)_2O$ with the Al₂O₃ Surface. The active site in the reaction of $(C_2F_5)_2O$ with Al_2O_3 consists of several components: (1) isolated hydroxyls which hydrogen bond with the ether to position the molecule for further reaction; (2) an oxide anion which bonds with the α -carbon of the ether fragment, forming adsorbed fluorocarboxylate; (3) isolated hydroxyls which donate hydrogen atoms to adsorbed carboxylates; and (4) cus aluminum atoms which abstract fluorines from the adsorbed carboxylates. The active site described is better defined by the Peri model because the activity of a larger section of the surface can be estimated. It is entirely possible that the octahedral and tetrahedral coordination of cus aluminum described by Knozinger accurately describes the geometry of the aluminum atoms within the active site. The presentation of equations representing the steps in the reaction mechanism is simplified by not attempting to draw an active site as a complete unit. Instead, we include only the part of the active site involved in the particular step described.

The following steps can be postulated for the adsorption and thermal decomposition/desorption mechanism for the $(C_2F_5)_2O/Al_2O_3$ system studied here:

$$(C_2F_5)_2O(g)$$
 + HO $(C_2F_5)_2O$ HO $(C_2F_5)_2O$ (1)

There are many configurations of sites capable of interacting with the $(C_2F_5)_2O(g)$ molecule; however, only a portion of these sites will react further to form an adsorbed carboxylate. Initially, $(C_2F_5)_2O(g)$ reversibly hydrogen bonds to the Al₂O₃ surface, until a site with the proper conformation is identified.

Once the ether is positioned at an active site, several steps occur which produce adsorbed trifluoroacetate. (a) The $(C_2F_5)_2O$ molecule is cleaved, producing two fragments, F_3C-F_2C-O and F_3C-F_2C . The F_3C-F_2C fragment is assumed to return to the gas phase. However, we are presently investigating evidence possibly indicating the presence of adsorbed fluoroethoxy which could suggest another reaction involving this species. (b) The F_3C-F_2C-O reacts with an oxygen anion through the α -carbon producing adsorbed trifluoroacetate. (c) Abstraction by a cus aluminum of the two fluorine atoms on the α -carbon accompanies carboxylate formation. Steps b and c may be reversed or may occur simultaneously. Reaction 2 pictured above shows that fluoroformate is also produced initially from adsorbed (C₂F₅)₂O. The large amount of fluoroformate at 0.0833 h at 500 K in Figure 5 suggests this is accurate. However, it is also possible that fluoroformate is produced from a partially defluorinated carboxylate. Fluoroformate production from adsorbed (C₂F₅)₂O would necessitate the cleavage of CF₃ from the CF₃CF₂O fragment.



Adsorbed trifluoroacetate is successively alkylated as it is reduced by nearby isolated hydroxyls. Cus aluminum atoms are oxidized as they become saturated with fluorine atoms. If nearby isolated hydroxyls are not limiting, the carboxylate will become fully alkylated. Similarly, fluoroformate is reduced to alkyl formate. As hydrogen atoms are donated to the carboxylate, oxide anions are reformed. It is uncertain as to whether these sites are capable of bonding another ether molecule to the surface, as cus aluminum atoms in the vicinity of the newly formed oxide anion(s) may be limited in concentration. If more ether molecules are bound to the surface, it is unlikely that they would be reduced to the same extent as seen initially.

Conclusions

Ordinarily it has been assumed that ether compounds are stable and unreactive; in fact, poly(fluoro ethers) are widely used as lubricants. However, many of the poly(perfluoro ether) lubricants are extensively degraded under mechanical stress in the presence of heat or high-energy radiation. Therefore, the chemistry between the fluorinated lubricant and the surface is an important concern. Our studies suggest that a promising approach to improving the activity of fluoro ether lubricants is to protect oxidizing surface sites to inhibit degradation of the lubricant.

This report presents the following results of an infrared spectroscopic investigation of the chemistry of excess $(C_2F_5)_2O$ on an Al_2O_3 surface studied at 300 and 500 K:

(1) $(C_2F_5)_2O$ adsorbs on the Al₂O₃ surface via interactions with isolated hydroxyl groups. $(C_2F_5)_2O$ is cleaved, forming two fragments, F_3C-F_2C-O and F_3C-F_2C . Trifluoroacetate and fluoroformate are formed as the F_3C-F_2C-O fragment bonds to the Al₂O₃ surface through the α -carbon. Carboxylates are successively alkylated as nearby isolated hydroxyls donate hydrogen atoms, forming difluoroacetate, monofluoroacetate, alkyl acetate, and alkyl formate. Fluorine atoms are abstracted by cus aluminum atoms. The process regenerates surface oxide anions. The same reaction takes place at 300 and 500 K although at different rates.

(2) The pressure decrease measured in the sample cell at 300 K is evidence of the ether bonding to the surface prior to oxidation by the surface. However, the linear pressure increase measured at 500 K is evidence of the greater rate of decomposition and desorption of adsorbed species observed at higher temperature.

(3) The presence of fluoroalkene and fluoroalkyne is suggested by the appearance of peaks at 1726, 1740, and 2258 $\rm cm^{-1}$. These species result from the decomposition of existing surface species. However, the mechanism of decomposition of a fluorocarboxylate to an alkene or alkyne is still under investigation.

(4) The ratios of the initial rates of formation of the six carboxylate species fall into two groups. The rates of formation of trifluoroacetate, monofluoroacetate, and alkyl acetate as measured by the ratio of the integrated intensities of the v_{as} -(OCO) modes at 300 and 500 K average 0.79. Whereas, the initial rates of formation of difluoroacetate, fluoroformate, and alkyl formate average 1.14. The same reactions are occurring at both temperatures albeit at different rates. The ratios of the initial rates of formation of [alkyl acetate]:[monofluoroacetate] and [alkyl formate]: [fluoroformate] average 0.60 at 300 and 500 Κ.

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