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Effect of a Fluorinated Nickel Surface on the Decomposition of
Perfluorodiethoxymethane

by

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DEDICATION

To my family
for their love and support

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INTRODUCTION

Perfluoropolyethers (PFPEs) are a commercial class of lubricants that are widely used particularly in computer and aerospace industries [1-10]. For example, on computer disks, it is necessary to apply a thin layer of lubricant to prevent direct contact between the disk and the read-write head [2,6,7] to protect them from damage and ensure smooth operation. It is seen that minimal attenuation of infra-red (IR) radiation occurs with PFPE fluids and as such they have been used as lubricants within IR scanners on space craft [10]. Once these perfluoropolyether lubricants are applied there it is important to understand how they are held there and how readily they decompose.

Figure 1 lists some of the commercially available perfluoropolyethers with their structures. Each type listed is structurally different and its chemical stability and physical properties is slightly different. Krytox and Fomblin Y polymer chains contain pendant trifluoromethyl groups ($-\text{CF}_3$) and are non-linear molecules. Demnum and Fomblin Z contain no pendant group and are linear. Linear PFPEs show less viscosity temperature variations in comparison to the non-linear PFPEs [3]. Trifluoromethyl groups are acidic and prevent acid catalyzed cleavage of the ether linkage when present adjacent to the ether linkage. Krytox has a $-\text{CF}_3$ adjacent to every ether linkage and is the most shielded. Fomblin Y is partially shielded and Demnum and Fomblin Z are non shielded.

PFPEs have a wide range of molecular weights. Fomblin Z and Fomblin Y are co-polymers and have molecular weights ranging from 1000 to 10,000 and 8000 to 70,000 respectively. Krytox has n , the degree of polymerization ranging

<i>Tradename / Supplier</i>	<i>Structure</i>
<i>Fomblin Z15 / Montedison</i>	$CF_3O - (CF_2CF_2O)_n - (CF_2O)_mCF_3$
<i>Fomblin Y / Montedison</i>	$CF_3[(OCF_2CF(CF_3)_n(OCF_2)_n)_m]OCF_3$
<i>Demnum S200 / Daikin</i>	$F(CF_2CF_2CF_2O)_n - CF_2CF_3$
<i>Krytox 143AD / Dupont</i>	$F(CF(CF_3)CF_2O)_n - CF_2CF_3$

Figure 1: Common perfluoropolyethers and their structure

from 1 to 80 and has a molecular weight range of 435-13,500. Demnum polymers can be made to any specific molecular weight desired. Guarini *et al.* calculated the molar ratio of the repeat units and compared them with their NMR results. They found the $C_2F_5O:C_3F_7O$ molar ratio of 51:49 for Demnum, $CF_2O:C_2F_4O$ in a 45:55 molar ratio for Fomblin Z and $C_3F_6O:CF_2O$ in a 99.2:0.8 molar ratio for Fomblin Y. These values show good agreement with their NMR results [11]. Some of these perfluoropolyethers are available with a variety of end groups, such as alcohol, carboxylic acids, isocyanide, pipyranyl and ether.

Perfluoropolyethers are colorless and odorless fluids. They have excellent thermal and oxidative stability. It is seen that highly branched PFPEs are less oxidatively stable than the fewer branched or unbranched PFPEs [12]. It is also observed that impurities in PFPEs lower thermal and oxidative stability. Perfluoropolyethers have very low vapor pressures on the order of 10^{-11} Torr. Density of PFPE is about 1.9 g/mL. Viscosity of PFPE depends on the molecular weight, it increases with increase in molecular weight. Other properties include low volatility, non flammability, biological inertness, low surface tension, high specific gravity and resistance to radiation.

Studies on adsorption and chemisorption of various PFPEs have been done on both metallic and non metallic surfaces using XPS, ellipsometry, FT-IR, microcalorimetry and atomic force microscopy [13-17]. It is seen that the strength of attachment and hence the protective ability of the lubricants depends on the functional end group attached to the PFPE. However, in the presence of metals PFPEs tend to decompose at elevated temperatures. Because of their potential applications at high temperatures, the thermal stability and thermal degradation process of these material have been investigated extensively [18-23].

Thermal stability of small perfluoropolyether compounds have been studied by thermal desorption spectroscopy on a variety of surfaces. Only analogs of perfluoropolyethers are necessarily used because introduction into ultrahigh vacuum chambers requires relatively volatile perfluoroether. Reactivities and decomposition of fluorinated monoethers [24-26] and diethers [27-29] have been investigated on a variety of transition metal surfaces. A lack of reactivity of PFPE analogs have been observed on a variety of transition metals. Ng *et al.* observed no decomposition of a fluorinated ether in aluminum oxide film. On single crystals, Walczak *et al.* studied the effect of diethoxyethane ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$), diethylether ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$) and diethoxymethane ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-O-CH}_2\text{-CH}_3$). Some dissociation was observed on the surface [26,30]. However, the interaction of perfluorodiethylether and perfluorodiethoxyethane on Ru(001) studied by Walczak *et al.* and Leavitt *et al.* showed that very little (< 0.002 monolayers) dissociation occurs below 165 K [28,31]. Studies with perfluorodiethylether on Pt(111) also revealed no decomposition [24,29]. John *et al.* looked at perfluorodimethylether and perfluorodimethoxymethane on polycrystalline Fe and polycrystalline Al and found no evidence of decomposition by X-ray photoelectron spectroscopy (XPS) for samples cleaned mechanically or by sputtering with Ar ions followed by annealing [32]. It has been proposed earlier that a surface mechanically cleaned is more active than one that is cleaned by sputtering and annealing [21,33]. Previous research by Jenks *et al.* [34] on the interaction of PFDEM with nickel and oxygenated nickel surfaces also shows no decomposition on these surfaces. In all the cases molecular adsorption and desorption was found. Decomposition of perfluoropolyether generally does not occur below temperatures 570 K [23].

Significant decomposition however was seen at relatively low temperatures (470 K), when in contact with a Lewis acid material such as iron oxide [22], aluminum oxide or aluminum chloride [35].

Thermal decomposition of large perfluoropolyethers however has been observed. Napier *et al.* investigated the chemistry of perfluoro-1-methoxy-2-ethoxyethane, perfluoro-1-methoxy-2-ethoxypropane, and perfluoro-1,3-diethoxypropane on polycrystalline Fe [36,37]. In addition, they also studied perfluoro-1-methoxy-2-ethoxy ethane on oxygenated, polycrystalline Fe samples [38] and Au [36]. They are used as model compounds to represent large molecular weight structures that have the same functional group and yield the same result. A lack of reactivity for all surfaces at 118 K was noticed, but decomposition was observed on the clean Fe surface for large exposures when the surface was held at 165 K. The evidence for decomposition was formation of FeF_3 , which was identified by XPS. They propose that decomposition of the carbon backbone is followed by dissociation of the molecule. Lin et al. observed decomposition of Fomblin Z-dol lubricant molecules around 550-550 K. The rate of thermal desorption of mainly the CF_2O^+ and CFO^+ fragments was found to be maximum at 640 K [39].

PFPEs have been shown to oxidatively decompose at higher temperatures and to corrode metal through the formation of reactive degradation products. The decomposition of PFPEs in the presence of metals and metal oxides involves a relatively slow transformation of the metal or metal oxide to a fluoride followed by a rapid catalytic degradation of the PFPE in the presence of metal fluoride [12,19,20,22,40-42]. Kasai performed thermal degradation studies of commercial PFPEs in the presence of metal oxides and metal fluorides. He describes a mechanism for PFPE degradation where in Al_2O_3 surface is converted

to the more acidic AlF_3 surface. The mechanism of degradation is shown in Figure 2. The formation of AlF_3 results in chain scission of the perfluoropolyether which is because of the interaction of the molecule with the Lewis acid sites. Carré proposed a similar PFPE degradation mechanism, after wear tests, which involved the formation of FeF_3 by the interaction of PFPE with iron. His mechanism involves two steps. In the first step, degradation is initiated by high temperature interaction between PFPE and freshly formed metal surface. This reaction generates FeF_3 in catalytic amounts which acts as a strong Lewis acid. In the second step, FeF_3 catalyzes the scission of PFPE C-O bonds. This occurs at much lower temperatures than those required for the onset of thermal degradation. The degradation products in turn react with the iron surface forming FeF_3 . A subsequent PFPE degradation catalyzed by FeF_3 is suggested as a pathway for the PFPE degradation under boundary lubrication conditions. The proposed mechanism is autocatalytic [20]. A temperature in excess of 773 K is estimated to be required for the dehalogenation of PFPE by iron. The degradation mechanism of the PFPE oil with FeF_3 is shown in Figure 3. Carré and Markowitz proposed a mechanism involving two pathways. Cleavage occurring at the primary carbon-oxygen bond to form a ketone (pathway ii) and at the secondary carbon-oxygen bond to form an acyl fluoride (pathway i). Their results indicate that cleavage can occur in both directions forming FeF_4^- as the by-product. Chandler *et al.* found that degradation of Krytox MCO-71-6 on Ti is accelerated by TiF_3 corrosion products on Ti surface. Further experiments carried out on Ti alloy (4Mn, 4 Al) do not indicate a mere oxidation of weak end groups. The formation of AlF_3 from the alloy causes chain scission. This in turn acts as a

Figure 2: Mechanism of degradation of an acetal containing PFPE on AlF_3 at the Lewis acid site proposed by Kasai *et al.* [35].

Figure 3: Carré and Markowitz's PFPE degradation mechanism showing the reaction of PFPE with FeF_3 [19]

fluorinating agent that attacks the ether bonds in the polymer. Other thermal desorption studies carried out by several authors also verify the transformation to a metal fluoride [22,35,40,42-45].

Some other degradation studies include the reaction of halogenated hydrocarbon with a PFPE lubricant on Fe surface. It is seen that under conditions of extreme pressure, chlorinated hydrocarbon additive (CH_2Cl_2) dissolved in the lubricant thermally undergoes decomposition at the surface forming a protective layer of iron halide and carbon [46]. Thermal stability of perfluoropolyethers on carbon surfaces was studied by Vurens *et al.* They observed decomposition at the low temperature range and found both the substrate (amorphous carbon surface) and the end group ($\text{CF}_3\text{-CF}_2\text{-}$) to be important factors in the decomposition of thin films of perfluoropolyether on surfaces [47].

X-ray photoelectron studies (XPS) and ion surface scattering studies show evidence for the transformation to a metal fluoride [20,21,33,45]. Mori and Morales used XPS and found that the decomposition reaction of the acetal ($\text{-O-CF}_2\text{-O-}$) containing PFPE liquid was due to metal fluoride generated during sliding conditions. Their results show that once the metal oxide layer wears off, PFPE liquids react with the fresh metal surface. The product of this reaction is a layer of adsorbed fluorocarbon over a metal fluoride layer. As the sliding continues, the metal fluoride and the adsorbed fluorocarbon layer forms a wear debris and they notice COF_2 formation. This they conclude is due to the catalytic activity of the metal fluoride which acts as a Lewis acid. Their studies on the friction behavior of perfluorodiethylether on iron surfaces also show an Fe-F bond formation. They also note that the films are not simply composed of

inorganic fluoride species (FeF_2) but also contain organic fluoride and oxyfluoride moieties as well.

Earlier studies involving degradation of perfluoroethers on metal and metal oxide surfaces under ultrahigh vacuum (UHV) do not generally show any evidence of decomposition [24,26,28-32,34,36,37,48,49]. Hence, the initial catalytic transformation of the substrate to a metal fluoride has not been isolated in these model studies. Perhaps the kinetics and efficiency of the reaction hinders its detection under conditions typical of UHV. However, there is evidence that the transformation of the substrate to a metal fluoride is initiated by impurities. Acyl fluoride or partially fluorinated polyethers with protonated end groups have been studied as impurities by several authors [12,29,32,42]. John and Liang found that perfluoroalkylethers did not react with clean metal surface. They observed complete decomposition of the acyl fluoride when in contact with a clean aluminum surface. Aluminum fluoride and aluminum oxide were obtained as products of this decomposition. Since acyl fluorides are a by-product of PFPEs, the formation of which is seen to be catalyzed by the metal fluoride, they concluded that acyl fluorides play a vital role in the PFPE degradation. Dekoven *et al.* conducted friction studies of perfluorodiethylether on oxidized and clean polycrystalline Fe samples under UHV conditions and concluded that at 298 K, low level of reactivity observed may be due to the impurities in the perfluorodiethylether [48].

Purpose of Present Work

A number of surface studies have been carried out in an attempt to understand the reactions of PFPE lubricants on metals. Of the various pathways

proposed in the decomposition of the PFPEs most commonly, it is shown to involve formation of a metal fluoride and subsequent rapid degradation. In this study we attempt to isolate the degradation of a perfluorinated ether in the presence of metal fluoride. Some authors suggest that impurities in the PFPEs such as acyl fluoride or partially fluorinated polyethers are responsible for the initial transformation of the substrate to a metal fluoride which is followed by decomposition on the fluorinated surface [12,32,42,48]. Our approach is similar to that of Napier *et al.* where they observe fluoride formation on the metal surface as an evidence for the decomposition. Present work involves formation of a fluorinated surface and studying its effect on a simple PFPE analog, perfluorodiethoxymethane (PFDEM). PFDEM is chosen as a model compound because it contains an acetal group which is thought to be particularly reactive [22,45,50]. It is seen that degradation is particularly problematic for PFPEs with acetal linkages (-O-CF₂-O-) [3,18,21,22,33,45]. Also the vapor pressure of PFDEM is high (136.6 Torr at 273.2 K) which makes it suitable for introduction into a ultra-high vacuum (UHV) system. The effects are examined on a single crystalline surface, Ni(100) under UHV conditions. Earlier work on nickel and nickel oxide surfaces shows no evidence of decomposition. All experiments are carried out using a clean Ni(100) crystal as the sample under ultrahigh vacuum. Hard disk drives consist of a thin metallic layer typically of Co-Pt-Cu on a nickel surface. Hence nickel is chosen as the substrate under investigation. An increase in the reactivity of a surface due to the presence of defect sites have been observed [21,33]. The effect of defect sites, present on the fluorinated surface, on the decomposition of PFDEM is also examined by studying the partially annealed surface.

Earlier work included studying the chemistry of PFDEM at Ni surface. Thermal desorption experiments carried out show peaks which are consistent with the *in situ* mass spectrum of PFDEM. This indicates that PFDEM desorbs from the clean nickel crystal intact without reaction or dissociation. This enables us to distinguish clearly between the activity of fluorinated surface and the clean surface towards the defluorination of the PFPE analog.

EXPERIMENTAL

The experiments are performed in a stainless steel ultra-high vacuum (UHV) [51] chamber for which a base pressure of less than 6×10^{-11} Torr is achieved routinely. This chamber is discussed in detail elsewhere [49,52] and only its most relevant aspects are presented here. A differentially pumped ion gun serves to clean the sample by Ar ion bombardment. Surface cleanliness is monitored with an Auger Electron Spectrometer (AES). A UTI 100C Quadrupole Mass Spectrometer (QMS) in the chamber is used for the Thermally Programmed Desorption (TPD) studies that also monitor the gas composition. The chamber is also capable of other surface analytical techniques like Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectrometry (HREELS). LEED is generally used to get information on the structure of the near-surface region and HREELS is used for determining the bonding geometry and surface atom vibrations. The sample surface is capable of exposure to various gases through a stainless steel doser aimed directly at the surface.

A directional doser with a $2 \mu\text{m}$ conductance-limiting aperture is used to introduce perfluorodiethoxymethane and CF_3I into the UHV chamber. For both PFDEM and CF_3I , the units of exposure are Torr-s. These units are defined using the pressure behind the conductance-limiting aperture as monitored using capacitance manometer. A separate directional doser with a $20 \mu\text{m}$ conductance limiting aperture is used to expose the surface to XeF_2 . The chemicals introduced into the chamber by a variable leak valve are reported in units of Langmuir ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr-s}$). Dose amounts are estimated from the total chamber pressure as measured by the Bayard Alpert ion gauge and exposure time.

Experiments are carried out in an UHV environment. In order to study the properties of surface that are well characterized at an atomic level, it is necessary to have the composition of the surface constant over the duration of the experiment. This means that the rate of arrival of reactive species from the surrounding gas phase should be low. The concentration of atoms on the surface of a solid is in the order of 10^{15} cm^{-2} . To keep the surface clean for 1 s or 1 hr, the flux of molecules incident on initially clean surface must be less than $\approx 10^{15}$ molecules/ cm^2/s or $\approx 10^{12}$ molecules/ cm^2/s respectively. The flux, F , of the molecules striking the surface per unit area at a given ambient pressure, P , is given by the kinetic theory of gases [53]

$$F = \frac{N_A P}{\sqrt{2\pi M R T}}$$

or

$$F(\text{molecules} / \text{cm}^2 . \text{s}) = 2.63 \times 10^{20} \frac{P(\text{Pa})}{\sqrt{M(\text{g} / \text{mole}) T}}$$

or

$$F(\text{molecules} / \text{cm}^2 . \text{s}) = 3.51 \times 10^{22} \frac{P(\text{Torr})}{\sqrt{M(\text{g} / \text{mole}) T}}$$

Where

M is the average molar weight of the gaseous species,

T is the temperature and

N_A is the Avogadro number.

For instance, at a pressure of about 3×10^{-6} Torr, using the values $M = 28$ g/mole and $T = 300$ K, we obtain the value of $F \approx 10^{15}$ molecules/cm²/s. This means that at this pressure the surface is covered with one monolayer of gas within seconds (assuming that the incident gas molecule sticks). At a pressure on the order of 10^{-9} Torr, it may take 10^3 s before the surface is completely covered.

In practice, one usually wants to study a surface without worrying about contamination from ambient gases. Current surface science techniques can detect as low as 1% contamination of a monolayer. We therefore require ultra-high vacuum (lesser than 10^{-9} Torr) to maintain a clean surface for a reasonable time [54,55].

Also common UHV apparatus configurations offer the possibility of using liquid nitrogen cooling devices to lower the sample temperature to around 95 K. This in turn allows one to adjust high adsorbate coverages because the (thermally activated) desorption process is sufficiently slowed at these temperatures. Therefore, using UHV environment not only provides well defined structural conditions but also application of the whole variety of optical and particle impact (mostly electron) spectroscopy.

Nickel is spot welded to two tungsten rods for efficient resistive heating. The rods are in thermal contact with a cold finger cooled with liquid nitrogen. The crystal temperature is monitored with a W 5%Re-W 26%Re thermocouple spot welded to the back of the crystal.

Nickel Cleaning

A single nickel crystal, 1 mm thick and 1 cm in diameter, is cut from a boule grown at Ames Laboratory Material Preparation Center and polished to

within 0.5 degrees of the (100) face. The nickel single crystal is cleaned using cycles of sputtering and annealing. Argon ion sputtering is done at 500 K for 15 min. with the beam voltage set at 2 kV. This is followed by annealing to either 600 K or 1025 K, depending upon the experiment. The crystal is placed in front of the Auger spectrometer to check for impurities. The major contaminants are carbon, oxygen and sulfur. Impurity peaks are seen at 273 eV, 503 eV and 152 eV representing carbon, oxygen and sulfur respectively. Sulfur is removed by argon ion bombardment. Carbon is removed by holding the crystal at 900 K and admitting 0.6 L of oxygen ($1\text{L} = 1 \times 10^{-6} \text{ Torr-s}$) undirected through a leak valve. The surface is then subsequently annealed to 975 K. The oxygen treatment is repeated until no impurities are detected by AES. Care is taken to avoid vigorous oxidation/annealing cycles as they can result in the subsurface being oxidized and therefore altering the surface structure [56,57]. Oxygen pressure is never allowed to exceed $5 \times 10^{-9} \text{ Torr}$ for this reason. All experiments are carried out on the clean nickel crystal.

Chemicals

Perfluorodiethoxymethane (PFDEM), used in our experiments is not available commercially. A small amount of PFDEM, originally synthesized at Exfluor, was donated by Dr. W.R. Jones, Jr. from NASA-Lewis. Mass spectral and gas chromatographic analysis of the PFDEM performed at ISU Instrumentation Service Center reveal trace amounts of impurities identified as small chlorofluorocarbons. The major impurities appear to be 1,2-dichloro-1,1,2,2-tetrafluoroethane and 1,2,2-trichloro-1,1,3,3,3-pentafluoropropane. However, no residual chlorine was ever detected on the Ni sample with AES even after

repeated adsorption-desorption experiments [34]. Perfluorodiethoxymethane used has a purity greater than 98.5%. PFDEM is a colorless liquid at 300 K and forms a glass when cooled to -184° . Its vapor pressure at 273.2 K is 136.6 Torr. The temperature - pressure dependence [58] for PFDEM is given by the equation:

$$\log P_{Torr} = -1645 / T_k + 8.138$$

CF₃I was purchased from PCR Inc. which specifies a 99% purity. Further purification of both PFDEM and CF₃I is done under vacuum, prior to experiments daily by repeated freeze-pump-thaw cycles with liquid nitrogen. Xenon difluoride was obtained from Aldrich and is stated to be 99.9% pure. It is further purified before the start of each experiment by subjecting it to repeated freeze-pump-thaw cycles using a dry ice/acetone bath. XeF₂ has a vapor pressure of 4.5 Torr at 298 K although it is a solid at room temperature [59], so it can be easily introduced into the UHV chamber.

Argon with a purity of 99.99% and oxygen with a purity of 99.6% is used as obtained from Matheson Gas Products.

Temperature Programmed Desorption

Temperature programmed desorption is an invaluable tool for elucidating adsorbate-adsorbate interactions and surface reaction, products, kinetics and mechanisms. The sample is placed in front of the mass spectrometer and is generally heated at a linear rate [60]. The products that desorb are monitored using a quadrupole mass spectrometer which can be controlled using a computer to monitor the required mass to charge (m/e) ratios.

The thermal desorption spectra are recorded using a UTI 100 C quadrupole mass spectrometer located close to the sample. The temperature ramp is controlled by a feed back circuit [61] to obtain a linear heating rate of 3 K/s up to 1000 K. The quadrupole mass spectrometer (QMS) and the temperature controller are both interfaced to an IBM-AT computer. This arrangement provides rapid data collection for up to 8 masses in a single experiment [62]. The relative m/e intensities in the QMS are calibrated using CF_3I and comparing the resulting spectrum to the standard mass spectrum of CF_3I [63]. The desorption products from the sample manipulator are prevented from entering the ionizer by placing a shield with a 6 mm aperture in front of the mass spectrometer ionizer. In the experiments conducted the sample is cooled to liquid nitrogen temperature. After the adsorbate of interest is introduced into the chamber, the crystal is placed in front of the QMS and thermally programmed desorption studies are carried out.

RESULTS

The experimental results of the thermally programmed desorption studies carried out are discussed here. Figure 4 shows the *in situ* mass spectrum of perfluorodiethoxymethane (PFDEM) introduced through the doser. This spectrum is similar to the mass spectrum taken by Hohorst and Shreeve [58]. The most abundant species is $m/e = 119$ (CF_3CF_2^+) and the peak corresponding to $m/e = 69$ (CF_3^+) is about half the intensity. The ratio of $m/e = 69$ (CF_3^+) to $m/e = 119$ (CF_3CF_2^+) is 0.56 and that of $m/e = 50$ (CF_2^+) to $m/e = 47$ (CFO^+) is 0.72. Our main approach involves formation of nickel fluoride and subsequent exposure of PFDEM. A TDS experiment is then carried out and checked for the effect on the decomposition of PFDEM.

Formation of a Fluorinated Nickel surface

Formation of fluoride on transition metals have been studied using CF_3I . On nickel surface, experiments were carried out using CF_3I by Jensen *et al.* [64] and Myli *et al.* [65]. Myli and Grassian observed NiF_2 desorption into the gas phase near 790 K for exposures greater than 1.5 L. They also observed the NiF_2 peak shift to higher temperatures with increase in CF_3I exposures. Jensen *et al.* in their TPD studies detected Ni^+ , NiF^+ , NiF_2^+ for all naturally occurring Ni isotopes which indicates the NiF_2 formation. They noticed the desorption of NiF_2 at 885 K with I desorption. Saturation coverage of NiF_2 was obtained on exposing the surface to 200 Torr-s. of CF_3I . Initial experiments involved subjecting the clean Ni surface to a saturation exposure of CF_3I at 95 K. A thermal desorption experiment was run to gauge the amount of NiF_2 formed.

Figure 4: *In situ* mass spectrum of perfluorodiethoxymethane
($\text{CF}_3\text{-CF}_2\text{-O-CF}_2\text{-O-CF}_2\text{-CF}_3$)

Figure 5 shows the effect of CF_3I on a surface that is annealed at 1025 K. The various masses probed have the following m/e values : 19 (F^+), 20 (HF^+), 58 (Ni^+), 77 (NiF^+) 96 (NiF_2^+) and 127 (I^+). Some nickel fluoride formation was observed when 200 Torr-s of CF_3I is dosed on the nickel surface. Further experiments were carried out to enhance the amount of fluoride formed by using XeF_2 to fluorinate the surface.

Studies using XeF_2 as a fluorinating agent have been done earlier. Interaction of XeF_2 on sapphire to form a fluoride was investigated by Hills using XPS [66] . Also using infrared reflection absorption spectroscopy (IRRAS), XeF_2 was shown to form a fluoride on silicon surface [67]. Formation of a fluoride on transition metal surfaces have been carried out by a few authors using XeF_2 . Loudiana *et al.* studied the electron enhanced growth of silver fluoride on a silver surface using AES and quartz crystal microbalance (QCM) [68]. They observed greater fluorine uptake and enhancement in the rate of silver fluoride growth on a fluorinated silver surface exposed to XeF_2 as opposed to a clean silver surface [68]. Similar results were also obtained by McIntyre and McTaggart [69]. They studied the rate of growth of films of silver fluoride on a silver surface using an electrical discharge. Figure 6 shows the *in situ* mass spectrum of XeF_2 . The major components are the Xe^+ ($m/e = 132$) and the Xe^{++} ($m/e = 66$) species. Other main fragments seen are XeF^+ ($m/e = 151$), F^+ ($m/e = 19$), XeF_2^+ ($m/e = 169$) and XeF^{++} ($m/e = 75.5$). This spectrum agrees closely with the mass spectrum of XeF_2 obtained by Loudiana *et al.* [70] . Our experiments show that multiple exposures of XeF_2 on Ni produce lesser amount of nickel fluoride than a fluorinated surface obtained from exposure to CF_3I and a subsequent exposure to TPD results using a 30 Torr-s XeF_2 exposure are shown in Figure 7 for a surface

Figure 5: Thermal Desorption Spectra of 200 Torr-s of CF_3I on $\text{Ni}(100)$ on a surface annealed at 1025 K

Figure 6: Mass spectrum of xenondifluoride taken *insitu*

Figure 7: Thermal Desorption Spectra showing the relative amounts of nickel fluoride obtained in the experiments indicated.

annealed at 600 K. The three spectra shown correspond to a 30 Torr-s exposure of XeF_2 at 225 K, a 200 Torr-s exposure of CF_3I followed by an XeF_2 dose at 225 K, and two subsequent 30 Torr-s exposures of XeF_2 at 225 K. Our fluorinated surface is prepared by first exposing our sample to 200 Torr-s CF_3I . It is then flashed to 600 K to remove the residual CF_3I and CF_x species [64]. This is then exposed to different amounts of XeF_2 at 225 K to avoid the presence of condensed XeF_2 . Below 225 K, evolution of XeF_2 in the TPD experiments is apparent. The desorption temperature of XeF_2 with a peak temperature of 205 - 220 K, is consistent with the known heat of sublimation of XeF_2 of 13.2 kcal/mol [59]. Therefore, desorption in this region is due to the desorption of multilayers of condensed XeF_2 . Fluorinated surfaces, for both a clean nickel surface annealed at 600 K and that annealed at 1025 K, were obtained in a similar fashion. Thermal desorption spectra for a 90 Torr-s exposure of XeF_2 is shown in figure 8. The various masses monitored are as indicated in the figure. Figures 9 and 10 show the plots of 200 Torr-s of CF_3I exposure followed by varying amounts of XeF_2 exposure vs. the peak area corresponding to $m/e = 77$, for surfaces annealed at 600 K and 1025 K respectively. A dramatic increase in the amount of fluoride formation is seen. This increase is relative to the amount of XeF_2 dosed on the surface. After a rapid initial increase, the curve plateaus on further XeF_2 exposures. Two different points on the curve are used for the experiments indicated here. A 30 Torr-s exposure, which lies on the rising part of the curve and a 90 Torr-s exposure, which lies on the plateau are chosen to represent the curve.

Figure 8: Thermal Desorption Spectra of 200 Torr-s of CF_3I followed by 30 Torr-s exposure of XeF_2 on Ni(100) surface annealed at 1025 K.

Figure 9: Amount of nickel fluoride as a function of XeF_2 exposure on a Ni(100) surface annealed at 600 K

FIGURE 10: Amount of Nickel fluoride as a function of XeF_2 exposure on a Ni(100) surface annealed at 1025 K

Interaction of PFDEM with a Fluorinated Nickel Surface

When a fluorinated surface, obtained from an exposure of 200 Torr-s of CF_3I alone is subjected to varying amounts of PFDEM (up to a 1000 Torr), no increase in the nickel fluoride peak height is seen. This could be attributed to the small amount of the fluoride formation due to CF_3I which is insufficient to cause the decomposition of PFDEM.

Interaction of PFDEM with larger coverages of the fluorinated surface were also studied. When a fluorinated surface got by exposing initially to 200 Torr-s of CF_3I , flashing it to 600 K and subsequently exposing to varying amounts of XeF_2 to produce more nickel fluoride, is further subjected to 200 Torr-s PFDEM at a crystal temperature of 600 K, no additional nickel fluoride formation is seen. Figures 11 and 12 show the thermal desorption spectra of the various experiments performed on the surface annealed at 600 K. Figure 11 shows the experimental results of a 90 Torr-s exposure of XeF_2 and Figure 12 shows the results of a 30 Torr-s exposure of XeF_2 . Figures 11a and 12a show a small amount of fluoride formation when the crystal is exposed to 200 Torr-s of CF_3I at 95 K. Figures 11b and 12b show an increase on using XeF_2 to form the fluoride. No fluoride formation is seen when the crystal is exposed to 200 Torr-s PFDEM alone in either case. Consistent results were obtained when the fluorinated surface got by coadsorption of CF_3I and XeF_2 is subjected to 200 Torr-s PFDEM. No additional nickel fluoride formation was seen on both, the low coverage and high coverage, of XeF_2 . Similar experiments conducted on a surface annealed at 1025 K are shown in Figures 13 and 14. Even on this surface lack of reactivity of PFDEM towards fluoride contribution is seen. The peak temperature for a 90 Torr-s

Figure 11: Thermal desorption spectra of various experiments indicated on a Ni(100) surface annealed at 600 K for a 90 Torr·s exposure of XeF_2 probing NiF^+ fragment (m/e 77)

Figure 12: Thermal desorption spectra of various experiments indicated on a Ni(100) surface annealed at 600 K for a 30 Torr·s exposure of XeF_2 probing NiF^+ fragment ($m/e = 77$)

Figure 13: Thermal desorption spectra of various experiments indicated on a Ni(100) surface annealed at 1025 K for a 90 Torr·s exposure of XeF_2 probing NiF^+ fragment (m/e 77)

Figure 14: Thermal desorption spectra of various experiments indicated on a Ni(100) surface annealed at 1025 K for a 30 Torr·s exposure of XeF_2 probing NiF^+ fragment (m/e 77)

exposure is shifted to a higher temperature from a 30 Torr-s exposure as seen from the figures.

Effects of Partially Annealed Vs Annealed Surface

Even though there is no contribution towards the formation of nickel fluoride on exposure to PFDEM observed on either surface, viz. surface annealed to 600 K only and surface annealed to 1025 K, the amount of nickel fluoride formed in each of these surfaces varies. Figure 15 shows the NiF^+ peaks (mass 77) on a nickel surface annealed at 600 K and 1025 K as indicated. Meaken [71] and Leamy *et al.* [72], have demonstrated that more open porous surface enables species to diffuse through them. The sticking probability is substantially high in atomically rough surfaces than smooth samples. Rough surfaces are chemically more active than flat surfaces at a given temperature. Thermal desorption studies clearly indicate that adsorbed atoms and molecules have higher heats of adsorption at defect sites on the surface [73]. The sensitivity of bonding to a surface structure leads to sequential filling of adsorption sites as coverage is increased, with the sites of highest adsorption energy filling first.

Figure 15: Thermal desorption spectra of NiF^+ fragment (m/e 77) showing the relative amounts of nickel fluoride formation on a surface annealed to 600 K and a surface annealed to 1025 K

DISCUSSION

Our experiments involve exposing the NiF_2 surface, obtained from CF_3I dose, to varying amounts of XeF_2 . Enhanced NiF_2 growth was observed as a function of XeF_2 exposure. The crystal is flashed to 600 K between exposures. The amount of NiF_2 formed after an exposure to XeF_2 on a partially fluorinated surface obtained by exposure to CF_3I , bears a correspondence to the amount of XeF_2 exposure. TPD experiments show an enhancement of NiF_2 over that formed using CF_3I alone or two subsequent exposures of XeF_2 . At saturation exposures of XeF_2 , the amount of nickel fluoride formed is about 20 times the amount formed using CF_3I alone. This is similar to the experimental observations of Loudiana *et al.* who reported a substantial increase in the amount of fluoride formation when a substrate fluorinated by other means is exposed to XeF_2 . This clearly indicates that CF_3I alone is not an efficient fluorinating agent.

The effect of the fluorinated surface is studied on PFDEM by monitoring the amount of NiF_2 formed using Thermally Programmed Desorption studies. PFDEM contains the acetal linkage which is highly susceptible to degradation [3,21,22,35,40,45,74,75]. Also, Kasai *et al.* have shown that an ethoxy end group is more powerful in degradation than a methoxy group [41]. This is due to the charge on the C atom. The carbon attached adjacent to the oxygen in a methoxy group has a much higher positive charge than the one in the ethoxy. The smaller net atomic charge on the ethoxy end group makes it more reactive. PFDEM contains an ethoxy end group as well which makes it all the more prone to degradation. Both nickel surface and the oxygenated nickel surface did not result in the decomposition of PFDEM [34]. A metal fluoride is more acidic than either

of those surfaces because of the high electronegativity of fluorine and is more reactive towards PFPE fluids. Interactions with Lewis acidic surfaces should increase the likelihood of dissociation [76] as should the use of an acetal-containing analog [45]. Also there is evidence for the decomposition of PFPEs to be initiated by the formation of metal fluoride [12,20,22,40-42,77,78]. It is also seen that greater the Lewis acidity of a surface, greater is the possibility of C-O bond rupture in the perfluoroethers [79]. Hence, the nickel fluoride substrate used in this study should enhance the reactivity of the surface towards PFDEM.

If the mechanism of decomposition involves extraction of fluorine from PFDEM or a C-C bond cleavage in PFDEM, it would result in the interaction with the surface adsorbed CF_3I moieties [64]]. This in turn, would contribute to NiF_2 formation and we would observe an increase in the NiF_2 peak. The dissociation energy typical of C-C bonds is about 607 kJ/mol and that of C-F and C-O is about 552 kJ/mol and 1076 kJ/mol respectively. Bond cleavage of C-C and C-F would be easier than C-O bond rupture. Our experiments show no increase in the amount of NiF_2 formed when treated with PFDEM. A maximum difference of only 2.4% is obtained between the surface exposed to PFDEM and the nickel fluoride surface. This could easily be due to the noise in the background and error in the points chosen for the area under the peak and is regarded as insignificant. We also see that this lack of increase in NiF_2 is independent of the initial fluorine coverage on the surface. This indicates that PFDEM does not contribute to the nickel fluoride formation which suggests that it does not involve extraction of fluorine to the surface leading to C-F bond cleavage. The perfluorinated ether by itself does not appear to initiate nor be the secondary cause of fluorination. If the extraction of fluorine was dependent on the metal fluoride bond strength, then

we should expect decomposition of the ether. Because, the bond strength of Ni-F is 110.5 Kcal/mole of NiF_2 which is comparable to that of Fe-F bond strengths in FeF_3 and FeF_2 where decomposition have been observed [36-38]. In FeF_3 , the Fe-F bond strength is 109 Kcal/mole and in FeF_2 it is 115 Kcal/mole. No metal fluoride bond rupture is seen in the nickel fluoride studied. This clearly indicates that the bond strength of a metal-fluoride is not a valid criterion for the decomposition of the perfluoropolyethers. Hence it could be true that impurities in the PFPEs initiate the fluorination of the surface as reported by John *et al.* It is also possible for the fluorinated surface to form a passivating layer as observed by Herrera-Fierro *et al.* The passivating layer thus created could prevent further attack of PFDEM on the surface.

Of the two different surfaces studied, as expected for a rough surface, surface annealed at 600 K shows a greater amount of nickel fluoride formation than the surface annealed at 1025 K. Surface annealed at 600 K is comprised of more steps than the surface annealed at 1025 K that is comprised of more terrace sites. The change in the amount associated with the stepped surface is due to the greater probability of dissociative adsorption of the reactant molecules at the ledge site. There would be more number of sites for the incorporation of impinging atoms. The reason for the increased dissociation efficiency is essentially because a lower activation energy is required at the ledges than on the terrace sites. Mori and Morales also showed that a mechanically rubbed surface is more reactive than a chemically sputtered and annealed surface. The increase in reactivity is attributed to the number of defect sites [21,33]. This is probably because the defect sites have a higher coordination available which leads to increased adsorption and dissociation[79].

Thermodynamic analysis was carried out on perfluoropolyethyleneoxide, whose mechanism of degradation was proposed by Kasai *et al.* Approximate bond dissociation energies of RC-F, C-OC, C=O are 931.36 kJ/mol, 277.4 kJ/mol and 532.2 kJ/mol respectively [80]. The enthalpy of formation for the reaction

was calculated to be -22.8 kJ/mol, which indicates that the product formation is favorable as proposed by the mechanism. The above degradation step has been carried out in an AlF₃ substrate. Donation of lone pairs from the p-orbital of oxygen to the Al in AlF₃ is further substantiated by the above calculation. The heats of formation of the products in Carré and Markowitz's mechanism (figure 3) were also calculated. ΔH values calculated for both products due to pathway (i) and products due to pathway (ii) are very similar. Products due to pathway (ii) is about 6 kcal/mol lower during the first step which involves the abstraction of fluorine from that carbon attached to the trifluoromethyl group (secondary carbon). The second step which involves the formation of the ketone is about 6 kcal/mol higher than the corresponding product obtained from pathway (i), which makes both the pathways equally favorable thermodynamically. The decomposition fragments of unbranched PFPAE and branched PFPAE proposed by other authors were also studied. The bond dissociation energies of the various

bonds involved in bond breaking/formation were taken into account and the feasibility of the proposed reaction mechanism was analyzed. For the reaction:

the formation of the decomposition products, the substituted alkane and the ketone is favored by 285.4 KJ/mol. The bond dissociation energy of C-F in CF₂ present adjacent to oxygen is about 996.5 KJ/mol and is typically the same for all perfluoropolyethers [Smart, 1992 #1142]. Calculations for a branched PFPE decomposition were also carried out. The proposed degradation products for R_f-CF-CF₃-O-CF₂-R_f is shown below.

This reaction is thermodynamically favorable by 237.8 KJ/mol. This makes the starting PFPE molecule stable by 27.6 KJ/mol compared to the unbranched PFPE. This is consistent with the properties of PFPE discussed earlier that greater the branching in a PFPE molecule, the more stable it is. It is also likely that the adjacent CF₃ group sterically shield the CF₂ group toward attack and the molecule tends to be more stable.

Theoretical studies suggest that dissociative chemisorption is at least thermodynamically favored for perfluorodimethyl ether interacting with Ni clusters [81]. Energy difference calculation by Bureau *et al.* between the chemisorbed and non-chemisorbed fragments show that dissociative chemisorption is exothermic. They calculated a Gibb's free energy change of -170 to -260 kJ/mol for perfluorodimethylether. Also, the cohesion energy of liquid PFPE's is small when compared to the gain in energy obtained upon dissociative chemisorption [81]. Therefore, they conclude that dissociative chemisorption would be clearly favored on a nickel surface containing reactive sites. Previous work suggests that while perhaps thermodynamically favored on Ni surfaces, dissociation must not be kinetically favored as no dissociation of perfluorodiethoxymethane, which as mentioned contains an acetal unit, on Ni(100) was observed [34]. The lack of contribution towards fluoride formation by the PFDEM does not rule out the possibility of PFDEM decomposing. It is only clear that it does not involve a fluoride intermediate. Our experimental results rules out the possibility of the PFPE degradation mechanism proposed by Carré and Markowitz. Their proposed mechanism involves the formation of FeF_4^- which is from the contribution of fluorine from the PFPE to the FeF_3 surface they studied. We do not see any additional formation of the fluoride. This indicates that the decomposition of perfluoropolyether is not autocatalytic as suggested by others [19,20,22]. If it involved an autocatalytic mechanism then the nickel fluoride formed on the substrate should enhance the decomposition of PFDEM and we would observe more NiF_2 on the surface. Also it does not appear that a simple metal-PFPE link would cause the metal-fluoride bonds to form. Of the two mechanisms discussed in this thesis, it is possible for our mechanism to

follow the one proposed by Kasai *et al.* The fluoride surface could be very well inducing the decomposition of the ether, but it does not involve the intermediate step of forming more metal fluoride indicated by Carré and Markowitz.

There is no evidence of NiF_2 formation even on defect rich fluorinated nickel surface upon exposure PFDEM. This is consistent with the results on defect surfaces obtained by other authors. The reaction of ZrO_2 with perfluorodiethylether does not show any effect on the reactivity or the adsorption strength [82]. The results on Ru (100) surface when treated with perfluorodiethylether, also do not show any change due to surface morphology [31]. John *et al.* also observed no difference when they compared their sputtered surface to their annealed one. They studied the interaction of perfluorodimethylether and perfluorodimethoxymethane on polycrystalline Fe and polycrystalline Al surfaces. All these results show that defect rich surface does not cause a change in the reactivity of the surface toward the PFPEs.

CONCLUSIONS

The effect of a fluorinated metal surface on an acetal containing PFPE analog has not been studied under ultra-high vacuum prior to this. The fluorinated surface is more Lewis acidic than the oxygenated or the clean nickel surfaces studied earlier. Acetal unit in PFPEs analogs is proposed as the critical moiety responsible for the decomposition of PFPEs and is thought to be particularly reactive in the presence of Lewis acids. Even when perfluorodiethoxymethane, a PFPE analog containing an acetal unit, is used, there is no contribution towards the metal fluoride formation even on a fluorinated nickel surface. Our work using temperature programmed desorption shows no contribution of PFDEM towards nickel fluoride on an NiF_2 surface obtained by CF_3I adsorption. Enhancement of nickel fluoride is seen by exposure to CF_3I followed by a subsequent exposure to XeF_2 . The amount of the fluoride formed is dependent on the amount of XeF_2 dosed. Even higher coverages of nickel fluoride also do not show any evidence of NiF_2 contribution from the PFDEM. There is no apparent effect on the result even on a rough surface although enhancement in the amount of NiF_2 is seen on CF_3I and XeF_2 coadsorption experiments relative to the smooth surface. Our results do not agree with the concept that a fluorinated surface might induce decomposition of PFPEs leading to additional fluoride formation on the surface. We also observe that the metal fluoride bond strength is not a legitimate concern for the decomposition of PFE lubricants. An impurity in the PFPEs might be the cause of initial surface fluoridation leading to the break down of PFPEs which could cause additional metal fluoride formation. It is clear that the reaction of PFPEs with metals does not involve a direct formation of a simple M-F bond.

Our results do not show any C-F bond cleavage of the fluorinated ether and do not support the autocatalytic mechanism proposed by others .

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