

Desorption Kinetics and Energetics of Monodisperse Fomblin Zdol from Carbon Surfaces

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Desorption is one of the mechanisms of lubricant loss from the surfaces of data storage media. This work has studied the desorption of monodisperse samples of a typical perfluoropolyalkyl ether lubricant, Fomblin Zdol, from the surface of graphite. Desorption is observed to occur molecularly through a first-order process with an energy barrier to desorption, $\Delta E_{\text{des}}^{\ddagger}$, that is independent of coverage but is dependent on molecular weight. The $\Delta E_{\text{des}}^{\ddagger}$ of 994 and 1329 g/mole fractions were found to be 128 ± 2 kJ/mol and 155 ± 2 kJ/mol, respectively. The pre-exponents, ν , of the first-order desorption rate constant were found to have values of $10^{19.6 \pm 0.3} \text{ s}^{-1}$ and $10^{21.1 \pm 0.3} \text{ s}^{-1}$ for the 994 and 1329 g/mole Zdol fractions, respectively. These results clearly reveal the chain length dependence of the $\Delta E_{\text{des}}^{\ddagger}$, and the high values of the pre-exponents are similar to those observed for desorption of other oligomeric species from graphite.

1. Introduction

The dynamics of oligomeric macromolecules adsorbed on surfaces is of fundamental importance to the understanding of interfacial properties such as lubrication and adhesion. Many industries rely on an understanding of interfacial phenomena to provide solutions to the challenging engineering problems that inhibit advances in their technologies. As an example, the magnetic storage industry uses thin films ($<20 \text{ \AA}$) of perfluoropolyalkyl ether (PFPE) lubricants deposited on thin ($\sim 100 \text{ \AA}$) amorphous carbon (a-C) overcoats to protect hard disks from mechanical damage due to contacts with the read-write heads flying over their surfaces.^{1–3} Maintaining the current growth rate in areal storage density requires that the distance between the disk and the read-write head (fly height) continue to decrease below its current value of $\sim 150 \text{ \AA}$.⁴ Speculation into the requirements for magnetic recording at areal storage densities of 1 Terabit/in² suggests that the magnetic separation must be decreased to $\sim 65 \text{ \AA}$.⁵ This advancement will place extreme constraints on the tribological performance required of the protective overcoat and lubricant layer applied to the surface of the magnetic storage medium. It is, therefore, essential to increase our fundamental understanding of the dynamic behavior of the lubricant films used at the head-disk interface to ensure the continued reliable operation of magnetic disk drive systems.

The most widely used PFPE for the lubrication of magnetic disk surfaces is Fomblin Zdol, which consists of a perfluorinated ether backbone terminated at either end by hydroxyl groups. It has the chemical structure



where the ratio x/y is typically between 2/3 and 1. These fluids have found use in hard disk drive applications as a result of their chemical inertness, high thermal stability, excellent lubricity, and extremely low volatility. Thin films of Fomblin Zdol are deposited onto the protective carbon overcoats which are generally hydrogenated or nitrogenated amorphous carbon (a-CH_x and a-CN_x) films.

One of the mechanisms of lubricant depletion from the surfaces of magnetic storage media is through desorption or

evaporation. Evaporation of low vapor pressure lubricants such as Fomblin Zdol from disk surfaces is negligible at room temperature but becomes significant at the temperatures reached inside a modern disk drive (60–80 °C).⁶ The issue of evaporation becomes increasingly important as the thickness of the applied lubricant films begins to approach molecular dimensions. This is an important problem and little is known about the kinetics or energetics of the desorption of oligomeric lubricants from surfaces. One of the issues that hinders the complete analysis of PFPE evaporation is the fact that these materials are generally applied to disk surfaces as polydisperse mixtures with a wide range of molecular weights. Fomblin Zdol used on computer disks has average molecular weights (M_n) ranging from 2000 to 5000 g/mole and polydispersities ranging from 1.4 to 1.7. As a result, the preferential desorption or evaporation of low mass fractions will occur initially and the average molecular weight of the lubricant remaining on the surface will increase with time. This suggests that a detailed understanding of the evaporation rate's dependence on molecular weight is needed. Another factor that prevents the development of a model to describe lubricant evaporation is the fact that the surfaces of the a-C films on which they are deposited are chemically heterogeneous and have a broad array of binding sites available for lubricant bonding.⁷ Problems arise because lubricants adsorbed on the different binding sites of the carbon overcoats have different energy barriers to desorption. Both the lubricant polydispersity and the surface heterogeneity contribute to the difficulty in interpreting quantitative measurements of lubricant desorption kinetics from disk surfaces.

Thermally programmed desorption studies of Fomblin Zdol on various carbon surfaces have been detailed in several reports. Lin et al. used TPD to study the thermally induced degradation of Fomblin Zdol ($M_n \sim 2000$ g/mole) adsorbed on an amorphous carbon film.⁸ Because of its high molecular weight the Fomblin Zdol decomposed during heating rather than desorbing from the surface. The threshold temperature reported for Fomblin Zdol decomposition was 500–550 K and is close to the intrinsic decomposition temperature of the molecule. Vurens and Mate also used TPD to explore the thermal stability of a polydisperse Fomblin Zdol film with a M_n of ~ 2000 g/mole adsorbed on both graphite and amorphous carbon.⁹ They too observed desorption features that they interpreted as arising from decomposition in the temperature range 500–800 K.

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Tyndall and Waltman have made isothermal measurements of the evaporation rates of both polydisperse¹⁰ and relatively monodisperse¹¹ PFPEs from a-CH_x. They measured the lubricant film thickness as a function of time and found that it decreased with kinetics that could not be fit with a simple first-order decay having a single-valued rate constant. The rate constant was observed to decrease with time (or lubricant film thickness). On the basis of these kinetic measurements, Tyndall and Waltman suggested that the evaporation of PFPE films from a-CH_x surfaces followed *nonclassical* first-order desorption kinetics having a rate constant that varied inversely with time; $k(t) = k_0(t/t_0)^{-1}$, where k_0 is defined as the initial rate constant. Alternately, they also showed that these evaporation kinetics could be described in terms of a classical rate constant which exhibits time-dependence due to the fact that the desorption energy, $\Delta E_{\text{des}}^{\ddagger}(\theta)$, is a function of film thickness or lubricant coverage on the surface. The dependence of the $\Delta E_{\text{des}}^{\ddagger}(\theta)$ on lubricant coverage can certainly arise from polydispersity effects and the initial selective desorption of the low molecular weight fractions. Tyndall and Waltman's experiments with monodisperse PFPE suggest that this is not an important issue in the sense that they still observed similar kinetics that they described with a nonclassical rate constant.¹¹ Alternatively, it is the case that the surfaces of the a-CH_x films are heterogeneous and expose adsorption sites with a range of adsorption energies.⁷ Molecules will desorb first from the sites with the lowest binding affinity and this will contribute to the observed thickness dependence of the apparent rate constant for desorption. Tyndall and Waltman explored this possibility by measuring desorption kinetics from both a-CH_x and a-CN_x films and observed the same time-dependent kinetics on both.

In this work, we present the first set of measurements of the desorption of highly monodisperse Fomblin Zdol from a carbon surface that is truly homogeneous, that of graphite. These measurements reveal that evaporation or desorption of Fomblin Zdol monolayers from graphite occurs molecularly with *classical* first-order desorption kinetics and a rate constant that depends only on temperature rather than time. Although graphite is not a perfect model for the a-C overcoat it does have the virtue of being homogeneous in that it is composed purely of sp² hybridized carbon atoms that can be kept perfectly free of oxidation under vacuum conditions. Films of Fomblin Zdol were deposited on the graphite surface at coverages ranging from submonolayers to many multilayers using a dosing system specifically designed for vaporizing and depositing materials having extremely low vapor pressures. Desorption rates from graphite have been measured for two fractions of Fomblin Zdol having M_n of 994 and 1329 g/mole and initial polydispersities <1.05. Desorption of both fractions is observed to occur molecularly through a first-order process with an energy barrier to desorption, $\Delta E_{\text{des}}^{\ddagger}$, that is independent of coverage but is dependent on the molecular weight. These are the first measurements that have eliminated both polydispersity and surface heterogeneity effects on the kinetics and energetics of Zdol desorption from a carbon surface. They reveal that the desorption kinetics on graphite can be described as a first-order process with a coverage independent $\Delta E_{\text{des}}^{\ddagger}$. More importantly, these measurements give the first insight into the chain length dependence of Fomblin Zdol desorption kinetics.

2. Experimental Section

All experiments were conducted in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of 10⁻⁹ Torr achieved through use of an ion-pump and titanium sublimation

pump. The chamber was also equipped with an ABB Extrel Merlin quadrupole mass spectrometer (QMS) for thermally programmed desorption (TPD) measurements. This instrument has a mass range of 1–500 amu and is capable of simultaneously monitoring up to five masses as a function of time during a TPD experiment. Dosing of the Fomblin Zdol onto the surface was accomplished using a device designed for deposition of high molecular weight, very low vapor pressure liquids and solids.

The substrate was a 12 × 12 × 2 mm piece of highly oriented pyrolytic graphite (HOPG). Prior to mounting, the sample was cleaved in air to expose the basal plane. The graphite was then mounted on a square piece of tantalum foil ~0.25 mm thick using electrically conductive silver epoxy (Aremco Co.). Two tantalum wires were spot-welded to the rear of the tantalum foil and mounted to the end of a manipulator capable of *x*, *y*, and *z* translation and 360° rotation. Once mounted the graphite could be cooled to ~120 K through mechanical contact with a liquid nitrogen reservoir at the end of the manipulator. In addition, the graphite substrate could be heated resistively at a constant rate using a computer to provide proportional-derivative temperature control. The temperature of the tantalum foil was measured using a chromel–alumel thermocouple spot-welded to its rear face. The temperature of the graphite sample was assumed to be that of its tantalum foil mount.

Ten samples of Fomblin Zdol with M_n ranging from 994 to 11 470 g/mole were obtained through supercritical fluid fractionation of Fomblin Zdol 2000. Only fractions having M_n of 994 g/mole and 1329 g/mole were used in this work. From this point on these two fractions will be referred to as Zdol 1000 and Zdol 1300. The values of M_n for each fraction were determined through NMR analysis by the Phasex, Inc. Polydispersities of the two fractions used were determined from GPC analysis by Jordi Associates and found to be <1.05. Although the Zdol samples were nearly monodisperse, each fraction required extensive degassing prior to use in order to remove low molecular weight fractions with very high vapor pressures. This outgassing procedure consisted of heating the Zdol samples in a glass vial under vacuum for ~12 h at temperatures ranging from 318 K (for Zdol 1000) to 373 K (for Zdol 1300). The purity of the Zdol fractions was further verified by measuring the heats of vaporization directly from multilayer desorption peaks generated in their TPD spectra and comparing these results with values reported in the literature.

Prior to each set of TPD experiments conducted with a given Fomblin Zdol fraction, the graphite sample was heated in a vacuum to ~1200 K to induce the desorption of any adsorbed contaminants. Surface cleanliness of the graphite sample has been assumed based on observations made in previous studies.^{12,13} In addition, desorption spectra were highly reproducible indicating that there was no contamination of the surface due to adsorbate decomposition. The desorption peaks for submonolayer coverages of heptane (C₇H₁₆) were used to assess the state of the surface reproducibility. During a normal TPD experiment using *n*-heptane the desorption temperature was consistently found to be 211 K, and the width of the desorption peak was <7 K. This result also indicates that the temperature of the graphite surface was highly uniform during heating.

Exposure of the graphite surface to the Fomblin Zdol fractions was performed using a high mass deposition source that has been described in detail elsewhere.¹⁴ This deposition source has allowed us to deposit Fomblin Zdol directly onto the graphite surface in UHV at coverages ranging from submonolayers to many multilayers by vaporization of the bulk Zdol fraction.

Apart from giving us the ability to conduct desorption experiments under controlled conditions, such vapor lubrication methods are also receiving attention as a potential alternative to the conventional dip-coating process used for lubricating disks.

Within the UHV chamber the graphite substrate was first positioned to face a stainless steel dosing tube from the high mass deposition source. The sample was then cooled to ~ 120 K prior to exposing its surface to vapor of the desired Zdol fraction. Following adsorption of the Zdol onto the graphite surface, the substrate was positioned approximately 2 cm from an aperture leading to the QMS and heated at a constant rate to the temperatures necessary to induce the desorption of all adsorbed species. During heating, the QMS was used to monitor the desorption rate of the adsorbed Fomblin Zdol and any decomposition products, if present. Under the conditions of our work, adsorption of both Zdol fractions was molecular and reversible with no indication of decomposition.

3. Results

In this work, we present the results of TPD measurements that show that the desorption of submonolayers of monodisperse Fomblin Zdol from a graphite surface can be described using a classical first-order rate expression. The rate of a first-order desorption process from a surface is expressed as

$$r = -\frac{d\theta}{dt} = k\theta = \nu \cdot \exp\left(-\frac{\Delta E_{\text{des}}^{\ddagger}}{RT}\right)\theta \quad (1)$$

where r is the rate of desorption, θ is the fractional coverage of the adsorbed species, k is the desorption rate constant, ν is the preexponential factor for desorption, and $\Delta E_{\text{des}}^{\ddagger}$ is the energy barrier to desorption. We present below the methods used to evaluate the order of the desorption reaction and the kinetic parameters ν and $\Delta E_{\text{des}}^{\ddagger}$ that describe the evaporation of Fomblin Zdol monolayers from graphite.

3.1 Reaction Order for Fomblin Zdol Desorption from Graphite. Prior to any detailed analysis of the kinetics of Fomblin Zdol desorption it is necessary to establish that the desorption process is indeed first-order and describable by eq 1. The order of the desorption reaction of the Fomblin Zdol fractions on graphite has been measured by performing TPD experiments using a constant heating rate, $\beta = 2$ K/s, and initial coverages of Fomblin Zdol ranging from submonolayers to many multilayers. Figure 1 shows the TPD spectra of Zdol 1300 initially adsorbed on the graphite surface at 120 K and different coverages. Deposition of the Fomblin Zdol fraction was performed by heating the bulk phase to 373 K in the high molecular weight doser. No decomposition of Zdol is expected at this temperature given previous reports indicating that its bulk decomposition temperature is ~ 600 K.¹⁵ The TPD spectra were generated by using the QMS to monitor the signal at $m/q = 81$ ($\text{CF}_2\text{CH}_2\text{OH}^+$) during heating. Several additional mass-to-charge ratios were monitored including $m/q = 61$ (CF_2CH^+), $m/q = 100$ (C_2F_4^+), and $m/q = 119$ (C_2F_5^+) in order to detect the desorption of any decomposition products, if present. The desorption signals at these m/q ratios occurred at the same temperatures suggesting that they are all due to desorption and electron impact fragmentation of the same molecule and that there is no decomposition of the Zdol 1300 on graphite during heating. No decomposition of either Zdol fraction was observed on the graphite surface.

At the lowest coverage, Zdol 1300 desorbs over a relatively wide temperature range (~ 60 K) and achieves a maximum rate of desorption at 387 K, as shown in Figure 1. As the Zdol 1300

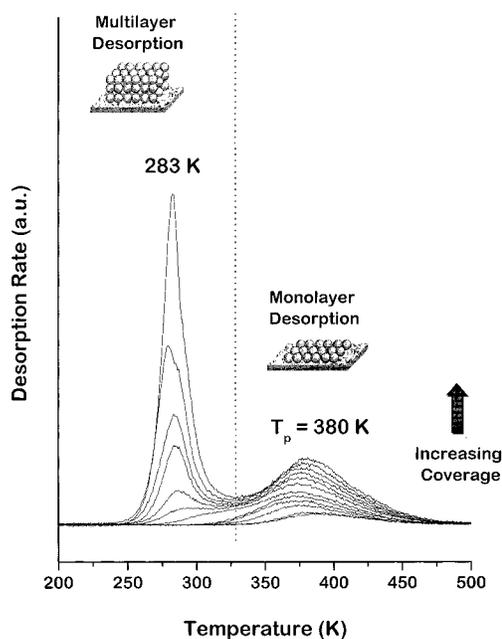


Figure 1. TPD spectra of Zdol 1300 adsorbed at various coverages on the graphite surface at 120 K. The desorption peak centered at ~ 380 K is assigned to desorption of the Zdol monolayer. The desorption feature at 283 K is assigned to desorption of Fomblin Zdol multilayers. The monolayer desorption temperature is roughly independent of coverage and indicates a first-order desorption process with a coverage-independent $\Delta E_{\text{des}}^{\ddagger}$. The spectra were generated using a mass spectrometer to monitor the signal at $m/q = 81$ ($\text{CF}_2\text{CH}_2\text{OH}^+$). The heating rate was 2 K/s.

exposure to the surface is increased, the desorption peak increases in intensity and shifts to slightly lower temperatures. At highest coverage the Zdol 1300 monolayer desorbs at 380 K. The fact that this peak temperature is fairly independent of coverage indicates that it is due to a first-order desorption process.¹⁶ As the Zdol 1300 exposure is increased further a second desorption feature grows in at ~ 283 K which indicates the onset of multilayer desorption. This low-temperature desorption feature continues to grow with increasing coverage and displays zero-order kinetics.

The heat of vaporization, ΔH_{vap} , has been used in this study as a basis for establishing the effectiveness of the techniques used to purify the Zdol fractions of any contaminants (such as low mass Zdol fractions). The value of ΔH_{vap} for Zdol 1300 has been estimated using the relation

$$\frac{d \ln r}{d(1/T)} = -\frac{\Delta E_{\text{des}}^{\text{mult}}}{R} \quad (2)$$

to determine the multilayer desorption energy, $\Delta E_{\text{des}}^{\text{mult}}$, from the leading edge of the multilayer desorption peak which exhibits zero-order desorption kinetics. The value of the $\Delta E_{\text{des}}^{\text{mult}}$ should be close to the heat of bulk vaporization, ΔH_{vap} , of the Zdol fractions. The data for the desorption of the Zdol 1300 multilayer are presented in Figure 2 and reveal that $\Delta E_{\text{des}}^{\text{mult}}$ of Zdol 1300 is 97 ± 1 kJ/mol. This is consistent with the value of $\Delta H_{\text{vap}} = 95$ kJ/mol for Fomblin Zdol 1300 reported by Stirniman et al.⁶ The agreement between the $\Delta E_{\text{des}}^{\text{mult}}$, and the value of ΔH_{vap} estimated by Stirniman et al. indicates that the purified Zdol 1300 sample is free of any low mass contaminants. Table 1 summarizes the multilayer desorption temperatures observed for the two Zdol fractions, the $\Delta E_{\text{des}}^{\text{mult}}$ determined in this study, and the ΔH_{vap} reported in the literature.⁶ The close agreement

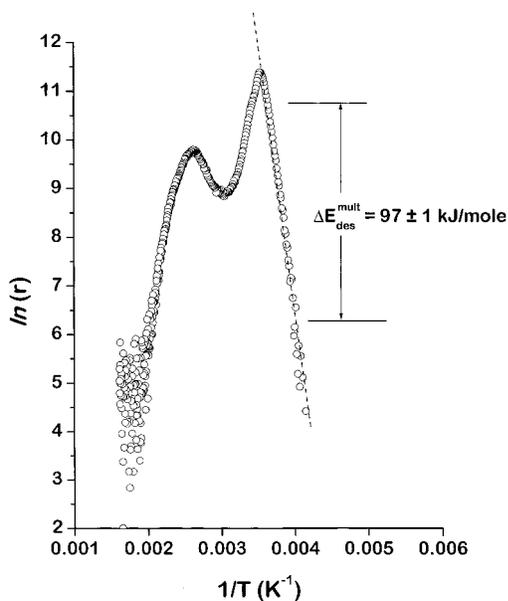


Figure 2. Arrhenius representation of the TPD spectrum for Zdol 1300 measured at highest coverage. A line has been fit to the leading edge of the multilayer desorption feature and measures the $\Delta E_{\text{des}}^{\text{mult}}$ for Zdol 1300 to be 97 ± 1 kJ/mol.

TABLE 1: Multilayer Peak Desorption Temperatures for the Monodisperse Fomblin Zdol Samples and Their Corresponding Desorption Energies, $\Delta E_{\text{des}}^{\text{mult}}$. The Purity of the Fomblin Samples Has Been Ascertained by Comparing the Measured Values of $\Delta E_{\text{des}}^{\text{mult}}$ with the ΔH_{vap} Reported in Ref 6

M_n (g/mole)	T_p (K)	measured $\Delta E_{\text{des}}^{\text{mult}}$ (kJ/mol)	ΔH_{vap} (kJ/mol)
994	266	85 ± 1	86.7 ^[6]
1329	283	97 ± 1	95.3 ^[6]

between the values of $\Delta E_{\text{des}}^{\text{mult}}$ and ΔH_{vap} for the two samples indicate that both are highly monodisperse. Equally important is the fact that the agreement confirms that our reported molecular weights are correct, or at least that they match those reported by Stirniman et al.

The dependence of the desorption spectra on Zdol coverage is similar for both fractions studied. In both cases, the desorption temperature of the monolayer is roughly independent of the Zdol coverage indicating that the desorption process is first-order and that there is little coverage dependence to the desorption barrier, $\Delta E_{\text{des}}^{\ddagger}$.¹⁶ The change in T_p in the submonolayer regime was 5 K for Zdol 1000 and 7 K for Zdol 1300. The small change in the T_p of the Zdols at these coverages indicates that there is very little coverage dependent interaction between the adsorbed molecules. These results are in complete agreement with a much more extensive study of the desorption of monodisperse alkanes from the graphite surface.^{14,17} Those alkanes covered the length range from 5 to 60 carbon atoms and span the range of molecular lengths of the Fomblin Zdols used in this study. On the basis of the observations made thus far in the current work it is reasonable to suggest that monodisperse Fomblin Zdols desorb from the graphite surface with first-order, coverage independent kinetics.

3.2 $\Delta E_{\text{des}}^{\ddagger}$ and ν for Fomblin Zdol Desorption from Graphite. TPD experiments performed with a constant heating rate and variable coverages of Fomblin Zdol on graphite have shown that the desorption kinetics are first-order in coverage. This result means that the desorption spectra of the Zdol fractions may be analyzed to give values for both ν and $\Delta E_{\text{des}}^{\ddagger}$.

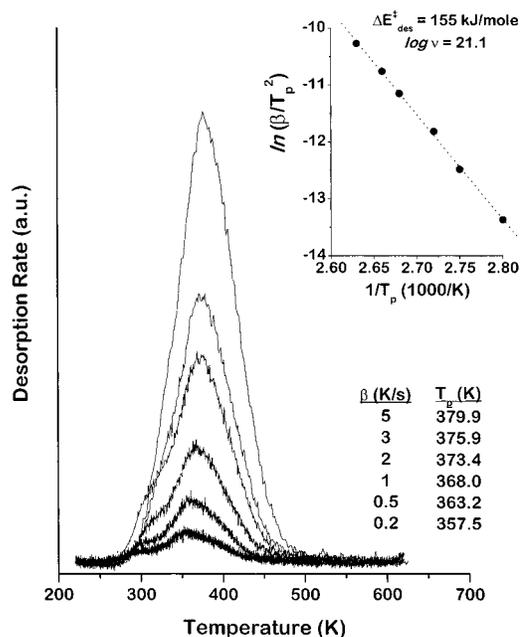


Figure 3. TPD spectra of Zdol 1300 measured at varying heating rates (β) for initial coverages of approximately one monolayer. Heating rates varying from 0.2 K/s to 5 K/s were used to desorb the Zdol monolayer. The spectra were generated using a mass spectrometer to monitor the signal at $m/q = 81$ ($\text{CF}_2\text{CH}_2\text{OH}^+$) during heating. The inset is a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the desorption of Zdol 1300 from the graphite surface. The slope of the linear fit has been used to estimate the $\Delta E_{\text{des}}^{\ddagger}$ for Zdol 1300 from graphite.

TPD spectra were recorded for Zdol 1000 and Zdol 1300 at various heating rates, β , using initial coverages of approximately one monolayer. The heating rates used in each set of experiments varied from 0.2 K/s to 5 K/s. Figure 3 illustrates the variable heating rate TPD spectra for Zdol 1300 generated by using the QMS to monitor the signal at $m/q = 81$ ($\text{CF}_2\text{CH}_2\text{OH}^+$). As the heating rate was increased, the desorption peaks shifted to higher temperatures. This increase of T_p with increasing heating rate is expected for a first-order desorption process.

Analysis of the heating rate dependence of the peak desorption temperature can be used to determine ν and $\Delta E_{\text{des}}^{\ddagger}$ independently. TPD data presented in the form $\ln(\beta/T_p^2)$ vs $1/T_p$ should yield a line with a slope equal to $-\Delta E_{\text{des}}^{\ddagger}/R$.¹⁶ Shown in the inset to Figure 3 is a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$, where T_p is dependent on the heating rate. A linear regression performed on the data in the inset of Figure 3 indicates that $\Delta E_{\text{des}}^{\ddagger} = 155 \pm 2$ kJ/mol for Zdol 1300. Figure 4 shows the variable heating rate TPD spectra for Zdol 1000 and the inset illustrates the fact that the dependence of the T_p on the heating rate can be adequately described by a classical first-order rate constant with $\Delta E_{\text{des}}^{\ddagger} = 128 \pm 2$ kJ/mol.

With the $\Delta E_{\text{des}}^{\ddagger}$ of the Zdol fractions measured, it is possible to evaluate the preexponential factors for desorption of each fraction of Fomblin Zdol. The preexponential factors for desorption, ν , may be estimated using Redhead's equation¹⁶ for first-order desorption kinetics

$$\nu = \frac{\beta \Delta E_{\text{des}}^{\ddagger}}{RT_p^2} \exp\left(\frac{\Delta E_{\text{des}}^{\ddagger}}{RT_p}\right) \quad (3)$$

where T_p depends on the heating rate, β . As indicated by eq 3, a preexponential factor for desorption may be calculated at each

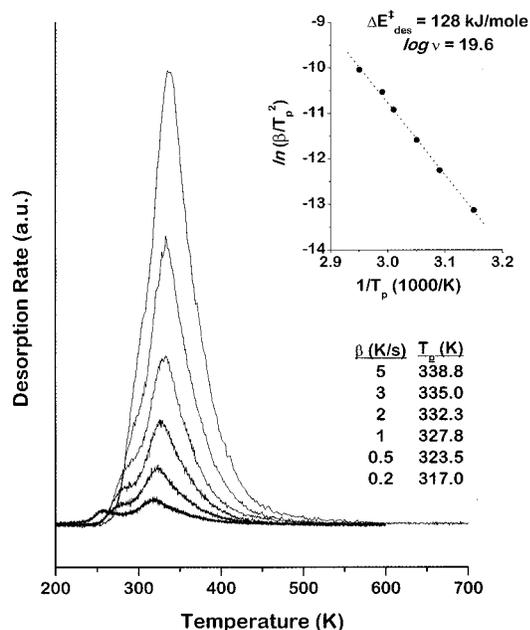


Figure 4. TPD spectra of Zdol 1000 measured at varying heating rates (β) for initial coverages of approximately one monolayer. Heating rates varying from 0.2 K/s to 5 K/s were used to desorb the Zdol monolayer. The monolayer desorption temperatures increase with increasing heating rate. The spectra were generated using a mass spectrometer to monitor the signal at $m/q = 81$ ($\text{CF}_2\text{CH}_2\text{OH}^+$) during heating. The inset is a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the desorption of Zdol 1000 from the graphite surface. The slope of the linear fit has been used to estimate the $\Delta E_{\text{des}}^\ddagger$ for Zdol 1000 from graphite.

heating rate. The averaged preexponential factors for Zdol 1000 and Zdol 1300 as measured using variable heating TPD experiments are $10^{19.6 \pm 0.3} \text{ sec}^{-1}$ and $10^{21.1 \pm 0.3} \text{ sec}^{-1}$ respectively. These are quite high values, however, they agree in magnitude with the pre-exponents measured for the desorption of high molecular weight alkanes from the graphite surface.^{14,17}

4. Discussion

One approach to minimizing PFPE loss by desorption from hard disk surfaces is the use of lubricants with increasing molecular weight or increasing average chain length. The longer chain lubricants will have a greater number of interactions with the disk surface and therefore have higher $\Delta E_{\text{des}}^\ddagger$. The tradeoff is, of course, that increased strength of adsorption generally leads to a decrease in mobility of the lubricant on the disk surface. Prediction of the lubricant desorption kinetics and their dependence on chain length requires an understanding of the problem of oligomer desorption from surfaces. Study of the desorption kinetics of alkanes from graphite has shown that the desorption energies do not scale linearly with chain length.^{14,17} Our study of the kinetics and energetics of Zdol desorption from graphite has probed the interactions of lubricant monolayers with the graphite surface. Below, we will place the results reported here in the context of prior investigations that have attempted to quantify the evaporation of long chain molecules from graphite surfaces and from a-CH_x films.

4.1 Energetics of Lubricant Evaporation from Surfaces.

It is clear from our data that the $\Delta E_{\text{des}}^\ddagger$ for Fomblin Zdol on graphite increases with increasing molecular weight. Although this result is expected, there is very little published experimental evidence demonstrating the molecular weight dependence of Zdol desorption from carbon surfaces. It is interesting to put into perspective the difference in the $\Delta E_{\text{des}}^\ddagger$ of Zdol 1000 and

Zdol 1300 on graphite. The $\Delta E_{\text{des}}^\ddagger$ for Zdol 1000 and Zdol 1300 are 128 ± 2 and 155 ± 2 kJ/mol, respectively, and thus differ by ~ 27 kJ/mol. Zdol is a random copolymer of ($\text{OCF}_2\text{-CF}_2$) and (OCF_2) monomers. If the assumption is made that the Zdol backbone is comprised entirely of (OCF_2CF_2) monomer units, then the Zdol 1000 and Zdol 1300 fractions used in this study would be comprised of an average of 7.0 and 9.9 monomer units, respectively. This translates into an increment of ~ 9.3 kJ/mol per (OCF_2CF_2) unit in the overall $\Delta E_{\text{des}}^\ddagger$ for the Fomblin Zdol molecules. The $\Delta E_{\text{des}}^\ddagger$ of longer chain Zdol molecules ($M_n > 1300$ g/mole) may scale linearly by this increment although the recent measurements of alkane desorption mentioned earlier suggest that the scaling may be nonlinear if measured over a wider range of chain lengths.^{14,17} It is also interesting to compare the $\Delta E_{\text{des}}^\ddagger$ of Fomblin Zdol with those of poly(ethylene glycols) [$\text{H}(\text{OCH}_2\text{CH}_2)_m\text{OH}$] on graphite which have been measured recently for a range of chain lengths that spans those of the Fomblin Zdols used in this work.¹⁸ The $\Delta E_{\text{des}}^\ddagger$ for poly(ethylene glycol) chains with $m = 1$ to ~ 8.7 were found to scale roughly linearly with chain length with an increase of 11.3 kJ/mol per (OCH_2CH_2) unit. As a final point of comparison the pre-exponents, ν , of the first-order rate constants for Zdol 1000 and Zdol 1300 desorption were found to be $10^{19.6 \pm 0.3} \text{ s}^{-1}$ and $10^{21.1 \pm 0.3} \text{ s}^{-1}$, respectively. These values are much higher than $k_B T/h \approx 10^{13} \text{ s}^{-1}$. Pre-exponents similar in magnitude have been observed for desorption of n -alkanes [$\text{C}_n\text{H}_{2n+2}$, $n = 5$ to 60],^{14,17} poly(ethylene glycol) dimethyl ethers [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_m\text{OCH}_3$, $m = 1$ to ~ 22] [20], and poly(ethylene glycols)¹⁸ from graphite. These high values of the desorption pre-exponents can be attributed to conformational isomerism in the desorbing species.

4.2 Kinetics of Lubricant Evaporation from Carbon Surfaces. In this work, we have shown that desorption of monodisperse Fomblin Zdol from the surface of graphite is describable by a simple first-order rate expression with a $\Delta E_{\text{des}}^\ddagger$ that is independent of coverage. This is not surprising since the desorption rates of longer chain molecules similar in nature to Zdol also exhibit simple first-order desorption kinetics on graphite. Desorption of n -alkanes,^{14,17} poly(ethylene glycol) dimethyl ethers,²⁰ and poly(ethylene glycols)¹⁸ from graphite was found to occur with first-order kinetics. The observation of first-order kinetics for desorption of poly(ethylene glycol) is particularly interesting in the context of the work reported here since the poly(ethylene glycol)s are hydrocarbon analogues of Fomblin Zdol. In addition, this work has shown that desorption of submonolayer coverages of Zdol 1000 and Zdol 1300 occurs quite rapidly in the temperature range ~ 330 – 390 K (60 – 120 °C). This temperature range can be encountered during normal operation of a disk drive and thus evaporation of Zdol lubricants with $M_n < 1300$ g/mole from disk surfaces can occur at a significant rate.

In view of the fact that desorption of monodisperse Fomblin Zdol from the surface of graphite occurs with a rate that is describable by simple first-order kinetics, it is important to examine the possible origins of nonclassical desorption observed in other work on the a-CH_x films. As mentioned previously, Tyndall and Waltman measured the evaporation kinetics of Fomblin Zdol from a-CH_x surfaces and found that the rate constant for Zdol evaporation decreased with time as the film thickness decreased. In their studies they fit the kinetic data with a rate constant that is *time-dependent* and has the form $k(t) = k_0(t/t_0)^{-1}$.^{10,11} Although this empirical form of the rate constant provided a good fit to their data, it is very hard to understand the physical origins of an intrinsic time dependence

and it is not needed to describe our data for Fomblin Zdol desorption from graphite.

The fact that the desorption experiments reported in this paper have used variable heating rates enables us to explore whether the desorption rate constant has an intrinsic time-dependence. The desorption of the Fomblin Zdols from graphite exhibits the behavior expected for a simple first-order rate constant in that the peak desorption temperature, T_p , depends on the heating rate, β . We can examine the consequences of a rate constant which is intrinsically time-dependent on the variable heating rate TPD experiment. If the heating rate is constant, $T = T_0 + \beta t$, then the desorption rate or the change in coverage with temperature is given by

$$r = -\frac{d\theta}{dt} = -\beta \frac{d\theta}{dT} = k\theta$$

If the rate constant were time-dependent with a form $k = k_0 t_0 / t$ then the change in coverage with temperature becomes

$$\frac{d\theta}{dT} = \frac{k_0 t_0}{T - T_0} \theta$$

The important point to note is that this is not dependent on the heating rate, β , and thus, the peak desorption temperature, T_p , will not depend on heating rate. The results of our experiments clearly reveal that the peak desorption temperature does depend on heating rate and thus that the desorption of Fomblin Zdol from graphite cannot be described in terms of a rate constant with an intrinsic time dependence of t^{-1} .

There are several possible origins for the fact that the desorption rate of Fomblin Zdol from the surfaces of a-CH_x films cannot be described with a classical first-order rate constant while the desorption of monodisperse Zdols from graphite can. As Tyndall and Waltman point out, it is possible that the $\Delta E_{\text{des}}^\ddagger$ in their system depends on the thickness or coverage of the lubricant film. Our work shows that the $\Delta E_{\text{des}}^\ddagger$ does depend on the chain length and thus that in a polydisperse sample of Zdol one would expect to observe a range of values of $\Delta E_{\text{des}}^\ddagger$ during the course of evaporation. Tyndall and Waltman's measurements with a sample having a fairly narrow molecular weight distribution (<1.08) also could not be described with a classical first-order rate constant. However, even such a sample has residual polydispersity and this was easily observable in measurements by Stirniman et al. of the evaporation kinetics of bulk Zdol samples with polydispersities of <1.04.⁶

One phenomenon that undoubtedly does give rise to a coverage dependent desorption rate constant in the work on a-CH_x and a-CN_x films is the fact that their surfaces are not homogeneous. In contrast, the surface of graphite is homogeneous, and the $\Delta E_{\text{des}}^\ddagger$ of the adsorbed molecules of Zdol are all identical (provided that all have the same chain length). The surfaces of a-CH_x films are known to be heterogeneous, and thus, it is not surprising that adsorbed molecules of Zdol have a range of values of $\Delta E_{\text{des}}^\ddagger$. This has been observed in a number of measurements of the desorption of small fluorinated ethers and alcohols from a-CH_x and a-CN_x surfaces.⁷ Thus, the desorption kinetics of long chain Zdols from the a-CH_x surface would not be describable by a classical first-order rate constant with a single value of $\Delta E_{\text{des}}^\ddagger$.

4.3 Implications for Data Storage Technology. Desorption of Fomblin Zdol from graphite was found to occur with first-order kinetics and a classical first-order, time-independent rate constant. Although the investigations reported here used graphite

as a substrate, the basic physics or mechanism of desorption should be the same for Fomblin Zdol from the a-CH_x and a-CN_x surfaces used to protect magnetic storage media. The only difference between these surfaces is that although graphite is homogeneous, amorphous carbon is heterogeneous and consists of a wide array of binding sites available for lubricant adsorption. This inhomogeneity would not be expected to change the reaction order for desorption but would impact the $\Delta E_{\text{des}}^\ddagger$ for Fomblin Zdol. Rather than describing the desorption process with a single desorption energy, one would have to account for that fact that molecules of Fomblin Zdol are bonded to a variety of sites having a range of adsorption affinities.

The $\Delta E_{\text{des}}^\ddagger$ measured in this work for desorption of Fomblin Zdol from graphite are also important from a different point of view. The values of $\Delta E_{\text{des}}^\ddagger$ directly determine the rate of evaporation for the Zdol lubricant. The $\Delta E_{\text{des}}^\ddagger$ is a measure of the strength of interaction of the molecule with the surface and is clearly dependent on the chain length. The values of $\Delta E_{\text{des}}^\ddagger$ also have implications for the diffusive properties of the lubricants on the disk surfaces. The implication of the chain length dependence of $\Delta E_{\text{des}}^\ddagger$ is that the diffusion kinetics will also depend on the chain length with the longer chain molecules exhibiting lower diffusion rates. To provide effective lubrication of the disk surfaces in future generation hard disk drives, the relative impact of chain length on both evaporation and diffusion must be considered.

5. Conclusions

The desorption kinetics and energetics of oligomeric PFPE lubricants such as Fomblin Zdol from the graphite surface have been shown to depend on chain length. If the lubricant is truly monodisperse and the surface is homogeneous then the desorption kinetics can be described with a classical first-order desorption rate constant. The values of the desorption energies increase with chain length but are independent of coverage.

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