

Kinetics of laser induced desorption and decomposition of Fomblin Zdol on carbon overcoats

Min Soo Lim, Andrew J. Gellman*

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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Abstract

Heat assisted magnetic recording (HAMR) on magnetic hard disks is being explored as a means of increasing the areal density of stored data beyond the limits of current technologies. HAMR will subject the magnetic media, the overcoat, and the lubricant on its surface to temperatures in the range 400–650 °C for periods of a few nanoseconds per pass of the read-write head. During such rapid heating events the lubricant is prone to decomposition and desorption from the surface, either of which lead to degradation of the lubricant film, jeopardizing the integrity of the stored data. Rapid laser annealing is known to bias the reactions of small molecules adsorbed on surfaces to favor desorption over decomposition. Analysis of the desorption and decomposition kinetics of perfluoropolyalkylether lubricants such as Fomblin Zdol shows that rapid heating to high temperatures favors desorption over decomposition for molecules with molecular weights of less than 3000. For higher molecular weight Fomblins decomposition is favored at the temperatures to be used for HAMR.
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1. Introduction

Magnetic recording has been the primary method for electronic data storage for the past 40 years because it provides a fast and easy way to read and write data. In the hard disk drive data is written to and read from a rotating disk whose surface is coated with a thin magnetic film which serves as the medium for storing data. Reading and writing is performed by a small read-write head that flies over the disk surface as it rotates. The magnetic medium is protected by a hydrogenated amorphous carbon overcoat ($a\text{-CH}_x$) with a thickness of $<100 \text{ \AA}$ and a $5\sim 20 \text{ \AA}$ thick lubricant film whose purpose is to minimize friction at the head-disk interface (HDI) [1,2].

The areal storage density, the number of data bits stored per unit area, has been increasing continuously for the past decade at a rate of 60% per year and has now reached densities in excess of 100 Gb/in.^2 [3]. This rate of increase is likely to be hampered in the near future by two significant problems. The first is the head-to-disk spacing which is

approaching the atomic scale. The read-write head is flying over the disk surface at a height of $\sim 50 \text{ \AA}$ [4]. Increasing the areal density can be achieved partly by decreasing the fly-height of the read-write head over the disk surface. Projections for the requirements of disk drives storing data at densities in excess of 1 Tb/in.^2 indicate that the head-disk spacing will be as small as 35 \AA [5,6]. The proximity of the read-write head to the disk surface will lead to more frequent high-speed contacts with the disk surface and probable damage to the surface. The other problem that will limit the growth of areal density arises from the magnetic storage medium and the difficulty of reducing the grain size to less than 10 nm. When the bits storing the data become too small they demagnetize rapidly at ambient temperatures, leading to loss of stored data. This is known as the super-paramagnetic limit. It is widely accepted that the current areal density of 100 Gb/in.^2 of conventional magnetic recording is approaching the limits imposed by superparamagnetism [7,8]. New recording techniques must be developed to surpass the super-paramagnetic limit of the magnetic medium and to allow continued increase in the areal storage density.

Heat assisted magnetic recording (HAMR) is one method that might allow magnetic recording to surpass the

* Corresponding author. Tel.: +1 412 268 3848; fax: +1 412 268 7139.
E-mail address: gellman@cmu.edu (A.J. Gellman).

superparamagnetic limit. HAMR combines the conventional magnetic recording technology of hard disk drives (HDD) and the optical recording technology used in CD re-writable (CD-RW) drives. As a consequence HAMR is also called 'hybrid recording'. To overcome the superparamagnetic limit associated with current magnetic media, HAMR would make use of media with coercivities that are too high for conventional read-write heads. In HAMR, a tiny laser light spot focuses onto a small region of the disk surface, rapidly heats the high coercivity magnetic medium to an elevated temperature ($>400\text{ }^{\circ}\text{C}$) thus temporarily lowering its coercivity to the point that writing is possible. HAMR is a promising recording technique that could increase areal storage densities beyond 1 Tb/in.^2 by using tiny magnetic grains with high coercivity but without sacrificing the thermal stability of the magnetic medium.

As with any new technology HAMR creates new problems that must be solved before it can be implemented. One such problem, which is the focus of this paper, is the effect of laser heating on the lubricants currently used to protect the disk surface. The current lubricants are perfluoropolyalkylether (PFPE) films that are $5\text{--}20\text{ \AA}$ in thickness and must last for the entire lifetime of the drive [9]. This thin lubricant layer is essential to protection of the magnetic media from damage arising from high speed contact of the read-write head with the disk surface. Molecular desorption, decomposition and diffusion of the polymeric lubricant films cause a depletion of lubricant from the disk surface. The depletion of this lubricant layer from the disk surface leads to a significant decrease in the wear durability of the disk. Thus, in order for HAMR to be developed to the point of practicality a lubricant must be found that can withstand periodic rapid laser heating to temperatures in excess of $400\text{ }^{\circ}\text{C}$.

The kinetics of desorption and reaction of molecules adsorbed on surfaces have been studied for many years [10, 11]. For the most part, however, these have been limited to the study of small molecules desorbing from or reacting on surfaces isothermally or during heating at relatively slow rates ($\sim 1\text{ K/s}$). The surface reactions that will occur during HAMR are complicated by the fact that the commonly used lubricants are large polymeric species and by the fact that the laser induced heating rates will be of order 10^{11} K/s . The desorption and decomposition mechanisms of small molecules on surfaces are well understood, even under conditions of rapid laser heating [12–14]. The desorption mechanism of long chain polymeric species such as perfluoropolyalkylether (PFPE) lubricants, however, is quite different from that of small molecules because a long chain lubricant molecule can adopt many different conformations on a surface all of which influence the kinetics of desorption [15,16]. The focus of this work is to couple our understanding of the kinetics and mechanism of polymer desorption from surfaces with our understanding of the effects of rapid laser heating on adsorbate desorption and decomposition. The goal is to

predict the behavior of polymeric lubricants under the conditions of HAMR operation.

PFPE lubricants have been widely used to lubricate commercial hard disk surfaces because they have chemical stability, high thermal stability, excellent lubricity, low viscosity at high molecular weights and extremely low volatility. Thus even at film thicknesses of $5\text{--}20\text{ \AA}$ they will lubricate the surface effectively for periods of years without decomposing or evaporating. Fomblin Zdol is one of the common PFPE lubricants and has the chemical structure



where the ratio x/y is typically between $2/3$ and 1 . It has a perfluorinated ether backbone that is terminated by hydroxyl groups at both ends. Desorption of polymeric species such as Fomblin Zdol from surfaces is a very complicated process. These molecules can adopt numerous different conformations as their segments attach and detach themselves from the surface in the process of going from the fully adsorbed to the desorbed state [17]. Measurements of Zdol desorption from the surface of graphite indicate that the apparent activation energy barrier for desorption is dependent on the chain length or the number of segments in the molecule [18]. The decomposition kinetics of Fomblin Zdol are, however, independent of the chain length [19]. Understanding the relative rates of Fomblin Zdol desorption and decomposition during laser heating on media surfaces is not only of fundamental interest but also of practical importance. The study presented in this paper explores the temperature dependence of the desorption barriers of Fomblin Zdols of varying molecular weights. Using these numbers and the known barriers to Zdol decomposition we predict the desorption and decomposition yields of the Fomblin Zdols during rapid laser heating.

2. Desorption and reaction kinetics during rapid laser heating of surfaces

At elevated temperatures molecules adsorbed on surfaces can either desorb or decompose depending upon the relative rate constants for each process (Fig. 1). At a constant temperature the relative rates of desorption and decomposition are dictated by the temperature and by the kinetic parameters for either process: the energy barrier, ΔE^{\ddagger} , and the pre-exponential factor, ν . During heating the relative yields of the two pathways will also depend on the heating rate (β). Previous laser induced thermal desorption (LITD) studies of small molecules show that rapid laser heating ($\beta \approx 10^{11}\text{ K/s}$) favors desorption over decomposition while heating at more conventional rates of $\beta \approx 1\text{ K/s}$ favors decomposition over desorption [12–14].

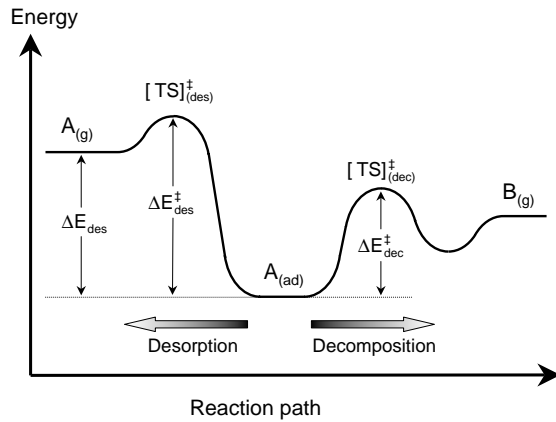


Fig. 1. Schematic potential energy surface showing two competing processes, desorption and decomposition, of an adsorbate (A) from the surface. During heating $A_{(ad)}$ either desorbs from the surface as $A_{(g)}$ or decomposes to form a product B which desorbs as $B_{(g)}$. The yield of each pathway depends on the values of the kinetic parameters for the decomposition and desorption rate constants.

The desorption and decomposition processes of small molecules from surfaces are often described by simple first-order kinetics with each rate constant having a single value for the activation barrier to desorption, $\Delta E_{des}^{\ddagger}$, or decomposition, $\Delta E_{dec}^{\ddagger}$, that is independent of coverage, θ . The process rates, r , are expressed as

$$r = -\frac{d\theta}{dt} = k\theta = \nu \exp\left(-\frac{\Delta E^{\ddagger}}{k_B T}\right)\theta, \quad (1)$$

where k is the rate constant, ν is pre-exponential factor, and k_B is Boltzmann's constant. $\Delta E_{des}^{\ddagger}$ or $\Delta E_{dec}^{\ddagger}$ are the differences in the zero-point energy of the adsorbed state and the zero-point energies of the transition states to either desorption or decomposition. The rate constant for each process can be written in an empirical Arrhenius form.

$$k'_{des} = \nu_{des} \exp\left(-\frac{\Delta E_{des}^{\ddagger}}{k_B T}\right) \quad (\text{for desorption}) \quad (2)$$

$$k'_{dec} = \nu_{dec} \exp\left(-\frac{\Delta E_{dec}^{\ddagger}}{k_B T}\right) \quad (\text{for decomposition}) \quad (3)$$

The desorption and decomposition of methanol on the Ni(100) surface have been studied extensively using both conventional heating at low rates and laser induced heating (LITD) [12]. The activation energy barriers for desorption and decomposition of methanol were found to be $\Delta E_{des}^{\ddagger} = 71.1$ and $\Delta E_{dec}^{\ddagger} = 57.6$ kJ/mol, respectively. The pre-exponential factors for desorption and decomposition of methanol were found to be $\nu_{des} = 10^{16} \text{ s}^{-1}$ and $\nu_{dec} = 10^{13} \text{ s}^{-1}$, respectively. Fig. 2 shows the Arrhenius plots of the rate constants vs temperature. The rate constants for desorption and decomposition increase as the temperature increases. At low temperature, however, the rate constant for decomposition exceeds that for desorption while at high

temperatures the rate constant for desorption exceeds that of decomposition. At a temperature of $T_c = 235$ K both rate constants are equal.

At low temperatures (< 235 K) the rate constant for methanol decomposition on the Ni(100) surface exceeds that for desorption. As a result one expects that adsorption of methanol on the Ni(100) surface at a temperature of 100 K followed by slow heating would lead to the decomposition. This is in fact what one observes. Methanol begins to deprotonate to methoxy and hydrogen at temperatures of ~ 160 K. During further heating one observes the dehydrogenation of the methoxy group and the desorption of H_2 and CO [20–22]. As Fig. 2 shows, however, at high temperatures the rate constant for methanol desorption from Ni(100) exceeds that for decomposition. Thus, if one adsorbs methanol at a low temperature (< 160 K) and then heats rapidly, the adsorbed methanol will not have sufficient time to decompose on the surface before the temperature reaches 235 K. At that point the adsorbed methanol will begin to desorb from the surface rather than decompose. This is what one observes during laser induced heating [12–14]. This example of the chemistry of methanol on the Ni(100) surface illustrates the fact that the heating rate can influence the yields of

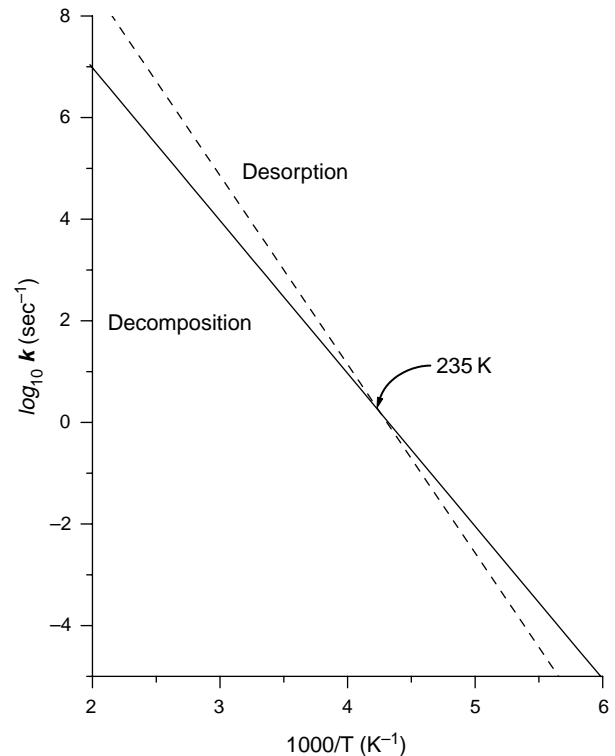


Fig. 2. The relation of $\log_{10}(k)$ vs $1/T$ is shown for methanol desorption (dashed line) and decomposition (solid line) processes from Ni(100) surface. The activation barriers for the two processes are $\Delta E_{des}^{\ddagger} = 71.1$ and $\Delta E_{dec}^{\ddagger} = 57.6$ kJ/mol. The pre-exponents are $\nu_{des} = 10^{16} \text{ s}^{-1}$ and $\nu_{dec} = 10^{13} \text{ s}^{-1}$, respectively [12]. The rate constants are equal at $T = 235$ K with decomposition dominating at lower temperatures and desorption dominating at the higher temperatures.

surface reactions and motivates our interest in the effects of rapid laser heating on the surface reactions of PFPE lubricants adsorbed on the surfaces of hard disks.

Analysis of the desorption and decomposition kinetics of PFPE lubricants is complicated by the fact that the desorption kinetics of long polymeric species are much more complex than those of small molecules. The desorption energies of small molecules such as methanol are assumed to be nearly constant and independent of temperature allowing the easy construction of linear Arrhenius plots. For oligomer desorption, however, the apparent desorption energies that one measures are temperature dependent and chain length dependent [15,16]. The chain length dependence of the apparent desorption energy is not surprising given that desorption involves the detachment of the oligomer from the surface along its entire length. The initial step of molecular decomposition, on the other hand, is a much simpler process which is localized to an individual chemical bond within the molecule and should not be dependent on chain length. These factors complicate the analysis of the relative importance of oligomer desorption and decomposition during laser induced heating.

3. Oligomer desorption from surfaces

Previous studies of the desorption of long chain oligomers such as alkanes, polyethylene glycols and Fomblin Zdol on graphite have provided the basic understanding of oligomer desorption from surfaces that will serve as the basis for our analysis of the effects of laser induced heating [15,17,18,23]. Those measurements show that desorption is a first-order process with a kinetic barrier that is independent of coverage, but dependent on chain length. The barriers to desorption, $\Delta E_{\text{des}}^{\ddagger}$, and the pre-exponential factors to desorption, ν_{des} , were determined using Redhead's equation and the peak desorption temperatures, T_p , measured using a range of heating rates [24].

$$\nu_{\text{des}} = \frac{\beta \Delta E_{\text{des}}^{\ddagger}}{k_B T_p^2} \exp\left(\frac{\Delta E_{\text{des}}^{\ddagger}}{k_B T_p}\right) \quad (4)$$

The desorption pre-exponential factors for the alkanes, polyethylene glycols and Fomblin Zdol were determined to be $10^{19.6 \pm 0.5}$, $10^{18.8 \pm 0.7}$, and $\sim 10^{20} \text{ s}^{-1}$, respectively, and are independent of chain length. The experimentally determined values of $\Delta E_{\text{des}}^{\ddagger}$ were shown to increase with chain length but non-linearly. The non-linearity in the chain length dependence of the $\Delta E_{\text{des}}^{\ddagger}$ arises from the complex nature of the desorption process for an oligomer and the fact that the desorption rate constants are measured at different temperatures as the chain length increases and the $\Delta E_{\text{des}}^{\ddagger}$ increases. The details of the oligomer desorption process as they apply to the problem at hand are described below.

The process of oligomer desorption from surfaces is complicated by the fact that such long, flexible molecules

can adopt many configurations in the process of detaching themselves from the surface. In the case of alkanes adsorbed on graphite surfaces there are numerous scanning tunneling micrographs which show that at low temperatures they adopt an all-*trans* configuration with all C–C bonds lying parallel to the surface [25,26]. This is a low entropy configuration. The process of desorption involves the random detachment of segments from the surface and the adoption of *gauche* conformations about detached C–C bonds [27]. These partially detached states have much higher entropy than the fully attached state. Thus, the process of desorption is not a simple elementary reaction step with a well-defined barrier. Instead it is a much more complex, multi-step process including a multiplicity of pathways leading from the fully attached state, through many possible partially detached states to the fully desorbed state. This process of alkane and polyethylene glycol desorption from graphite has been modeled successfully to predict the non-linear dependence of the measured values of $\Delta E_{\text{des}}^{\ddagger}$ on chain length [15,16].

The rate constant, k_{des} , used to model oligomer desorption from a surface has the form given by transition state theory [28]

$$k_{\text{des}} = \left(\frac{k_B T}{h}\right) \frac{q_{\ddagger}}{q} \exp\left(\frac{-\Delta E_{\text{des}}^{\ddagger}}{k_B T}\right) \quad (5)$$

where h is Planck's constant. For an oligomer the value of $\Delta E_{\text{des}}^{\ddagger}$ in this expression is the difference in zero-point energies of the fully attached state and the fully detached state. The terms q and q_{\ddagger} are the partition functions for the adsorbed state and the desorbed state. It is important to keep in mind that the partition function for the adsorbed oligomer, q , includes terms for all the partially detached states with *gauche* conformations. Given this expression for the rate constant it is important to keep in mind the fact that the empirical value of the $\Delta E_{\text{des}}^{\ddagger}$ that one determines by fitting experimental rate data to the empirical Arrhenius form of the rate constant is given by

$$\Delta E_{\text{des}}^{\ddagger} = -k_B \frac{d \ln(k_{\text{des}})}{d(1/T)}. \quad (6)$$

Prior analysis of alkane and polyethylene glycol desorption from graphite [17] has shown that the measured value of the $\Delta E_{\text{des}}^{\ddagger}$ for an oligomer such as Fomblin Zdol can be expressed as

$$\Delta E_{\text{des}}^{\ddagger} = I \left[\frac{q_{\text{tg}}^{\text{CC}} \Delta E^{\text{ss}} + (q_{\text{tg}}^{\text{CC}} - 1) \Delta E_{\text{tg}}^{\text{CC}}}{q_{\text{tg}}^{\text{CC}} \left(1 + q_{\text{tg}}^{\text{CC}} \exp\left(\frac{-\Delta E^{\text{ss}}}{k_B T}\right)\right)} \right] + J \left[\frac{q_{\text{tg}}^{\text{CO}} \Delta E^{\text{ss}} + (q_{\text{tg}}^{\text{CO}} - 1) \Delta E_{\text{tg}}^{\text{CO}}}{q_{\text{tg}}^{\text{CO}} \left(1 + q_{\text{tg}}^{\text{CO}} \exp\left(\frac{-\Delta E^{\text{ss}}}{k_B T}\right)\right)} \right] + \Delta E + k_B T \quad (7)$$

In this expression I and J are the numbers of C–C and C–O bonds in the oligomer. The quantity ΔE^{ss} is the segment-surface interaction energy associated with the adsorption of each of the C–C or C–O bonds with the surface. In this expression they have been averaged into one constant since they are not likely to be much different and we have no way of evaluating each independently. The quantity ΔE is a constant which would include effects such as the additional adsorption energy associated with the –OH endgroups of Fomblin Zdol. Finally the partition functions for the *trans-gauche* conformations about the C–C and C–O bonds are expressed as

$$q_{\text{tg}}^{\text{CC}} = 1 + 2 \exp\left(\frac{-\Delta E_{\text{tg}}^{\text{CC}}}{k_{\text{B}}T}\right) \quad (8)$$

where $\Delta E_{\text{tg}}^{\text{CC}}$ or $\Delta E_{\text{tg}}^{\text{CO}}$ are the energy differences of the *trans* and *gauche* conformations about each C–C or C–O bond. Note that Eq. (7) for the empirical or measured value of $\Delta E_{\text{des}}^{\ddagger}$ depends on both temperature and on the chain length of the oligomer. Given estimates for the physical parameters in this expression it is possible to evaluate the empirical $\Delta E_{\text{des}}^{\ddagger}$ and thus the desorption rate constant, k_{des} , over a wide range of temperatures and thus compare it to the rate constant for decomposition, k_{dec} .

4. Decomposition of Fomblin Z and Zdol on a-CH_x

Fomblin Z and Fomblin Zdol are the most common PFPEs used as lubricants on magnetic data storage disks. They have the same molecular backbone, but their end groups are different. Fomblin Z is terminated with trifluoromethyl (–CF₃) groups, while Fomblin Zdol is terminated with hydroxyl groups (–CF₂CH₂OH). In prior work we have investigated the decomposition kinetics of Fomblin Z and Zdol on amorphous hydrogenated carbon (a-CH_x) surfaces using temperature programmed reaction spectroscopy (TPRS) [19]. Disk samples coated with Fomblin lubricants having different molecular weights (MW = 4000 and 50,000) and different thickness (20 and 60 Å) were heated in vacuum while using mass spectrometry to detect desorbing species and measure their rates of desorption. The desorption of Fomblin decomposition products was detected in the temperature range 600–750 K. The results suggest that the decomposition kinetics for Fomblin lubricants on a-CH_x overcoats are independent of the type of end group and the chain length. The kinetic parameters for Fomblin decomposition were measured to be $\Delta E_{\text{dec}}^{\ddagger} = 114 \pm 6$ kJ/mol and $\nu_{\text{dec}} = 10^{9.6 \pm 0.3} \text{ s}^{-1}$, respectively. Note that the decomposition barrier, $\Delta E_{\text{dec}}^{\ddagger}$, is independent of chain length, while the measured desorption barrier, $\Delta E_{\text{des}}^{\ddagger}$, is dependent on chain length. This is not surprising given that desorption requires detachment of the entire length of the molecule from the surface while

Table 1
Fomblin Zdol characteristics and crossover temperatures

| Nominal MW | 1000 | 2000 | 3000 | 4000 | 5000 |
|---|------|------|------|------|------|
| MW (g/mol) | 1022 | 2048 | 3008 | 4034 | 4995 |
| OCF ₂ monomers (x) | 4 | 9 | 13 | 18 | 22 |
| OCF ₂ CF ₂ monomers (y) | 5 | 11 | 17 | 23 | 29 |
| C–C bonds (I) | 7 | 13 | 19 | 25 | 31 |
| C–O bonds (J) | 22 | 44 | 64 | 86 | 106 |
| Crossover temperature (K) | 209 | 423 | 594 | 778 | 946 |

decomposition is probably initiated by the dissociation of a single C–O or C–C bond in the PFPE chain.

5. Laser induced desorption and decomposition of Fomblin Zdol

The central issue to be addressed by this paper is the effect of laser induced annealing on the decomposition or desorption of Fomblin lubricants from surfaces. As indicated above, rapid laser induced heating of small molecules adsorbed on surfaces tends to favor desorption over decomposition even when the kinetic parameters favor decomposition at the low initial temperatures. In the case of Fomblin desorption from surfaces, however, one has to consider much more complex desorption kinetics than those used to describe desorption of small rigid molecules from surfaces. At this point the interplay between the effects of rapid laser heating and the complex Fomblin desorption process is not understood.

In order to understand the effects of laser induced heating on the surface reaction kinetics of Fomblin Zdol we have simulated these kinetics for a series of Fomblin Zdols having different molecular weights (nominal MW = 1000–5000). Actual molecular weights were selected, such that they are close to the nominal molecular weight and the ratios of OCF₂ and OCF₂CF₂ groups are in the range $x/y = 2/3$ to 1. The nominal and actual molecular weights of these Fomblins are listed in Table 1 with the number of C–O and C–C bonds.

The kinetic parameters measured in previous work were used to investigate the desorption and decomposition kinetics of Fomblin Zdol during laser induced heating. These are shown in Table 2. The energy differences between the *trans* and *gauche* conformations about C–C and C–O

Table 2
Kinetic parameters for Fomblin Zdol desorption and decomposition

| Desorption | Decomposition |
|------------------------------------|------------------------------------|
| $\Delta E_{\text{tg}}^{\text{CC}}$ | $\Delta E_{\text{dec}}^{\ddagger}$ |
| $\Delta E_{\text{tg}}^{\text{CO}}$ | ν_{dec} |
| ΔE^{ss} | |
| ΔE | |
| ν_{des} | |

bonds were found to be $\Delta E_{\text{tg}}^{\text{CC}} = 0.50 \text{ kJ/mol}$ and $\Delta E_{\text{tg}}^{\text{CO}} = 0.59 \text{ kJ/mol}$ from Waltman's ab initio calculations of the torsional energies about the C–C and C–O bonds in $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}_3$ [29]. The value of $\Delta E = 36.6 \text{ kJ/mol}$ [17] previously obtained for the desorption of polyethylene glycols from graphite was adopted to describe the desorption kinetics of Fomblin Zdol. Fomblin Zdol is structurally similar to polyethylene glycol except that the backbone of the Fomblins is fluorinated. Fluorination of the backbone does reduced the net desorption energy. The measured desorption energy of Fomblin Zdol 1000 from graphite is $\Delta E_{\text{des}}^{\ddagger} = 128 \pm 2 \text{ kJ/mol}$ [18] while that of polyethylene glycol of the same nominal chain length is $\Delta E_{\text{des}}^{\ddagger} = 167 \pm 4 \text{ kJ/mol}$ [17]. The difference must be due to different segment-surface interaction energies, ΔE^{ss} , for the fluoroether and hydrocarbon ether backbones. The value of ΔE^{ss} has been calculated using Eq. (7). The value of ΔE was taken to be the same as that found for polyethylene glycol and the desorption temperature of Fomblin Zdol 1000 from graphite is $T_p = 332.3 \text{ K}$ [18]. Using these values and Eq. (7) we obtain we obtain $\Delta E^{\text{ss}} = 4.4 \text{ kJ/mol}$. The pre-exponential factors, ν_{des} , for oligomer desorption from surfaces have been found to be independent of chain length. For Fomblin Zdol 1000 the desorption pre-exponent was measured to be $\nu_{\text{des}} = 10^{19.6 \pm 0.3} \text{ s}^{-1}$ and this value has been adopted to describe the desorption of Fomblin Zdols having

different molecular weights. These kinetic parameters are used with Eqs. (2) and (7) to determine the rate constants for Fomblin desorption.

$$\ln k_{\text{des}} = \ln \nu_{\text{des}} - \frac{\Delta E_{\text{des}}^{\ddagger}}{k_B T}$$

$$= \ln \nu_{\text{des}} - \frac{1}{k_B T} \left[I \left\{ \frac{q_{\text{tg}}^{\text{CC}} \Delta E^{\text{ss}} + (q_{\text{tg}}^{\text{CC}} - 1) \Delta E_{\text{tg}}^{\text{CC}}}{q_{\text{tg}}^{\text{CC}} (1 + q_{\text{tg}}^{\text{CC}} \exp(-\Delta E^{\text{ss}}/k_B T))} \right\} \right. \\ \left. + J \left\{ \frac{q_{\text{tg}}^{\text{CO}} \Delta E^{\text{ss}} + (q_{\text{tg}}^{\text{CO}} - 1) \Delta E_{\text{tg}}^{\text{CO}}}{q_{\text{tg}}^{\text{CO}} (1 + q_{\text{tg}}^{\text{CO}} \exp(-\Delta E^{\text{ss}}/k_B T))} \right\} + \Delta E + k_B T \right] \quad (9)$$

Eq. (9) reveals the complex dependence of the desorption kinetics on both temperature and chain length. Previous studies suggest that the decomposition kinetics of Fomblin Zdol on a- CH_x are independent of chain length. Eq. (3) has been adopted to describe the rate constant for decomposition of Fomblin Zdols, k_{dec} . The kinetic parameters for decomposition reported previously have been used in this work. The kinetic parameters for desorption and decomposition of Fomblin Zdols shown in Tables 1 and 2 have been used to evaluate the respective rates constants using Eqs. (3) and (9). Fig. 3 compares the desorption and decomposition rate constants for Fomblin Zdol 1000 in the form $\log(k)$ vs $1/T$ and illustrates the effects of chain flexibility on the desorption kinetics. The decomposition kinetics exhibit Arrhenius-like

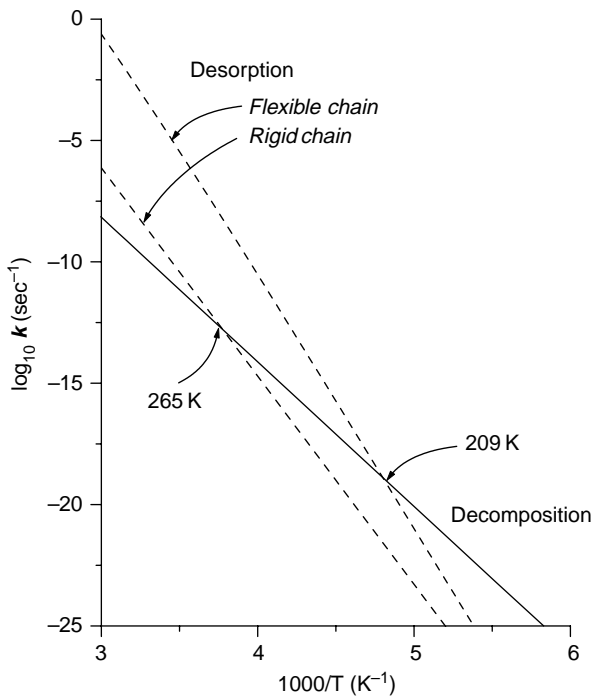


Fig. 3. Rate constants in the form $\log_{10}(k)$ vs $1/T$ for decomposition of Fomblin Zdol 1000 on an a- CH_x surface (solid line) and for desorption as either a rigid or flexible chain (dashed lines). The effects of chain flexibility on the desorption kinetics are to reduce the effective desorption barrier or increase the desorption rate constant above what one would predict for the rigid chain. This in turn reduces the temperature at which one observes a crossover of the rate constants for desorption and decomposition.

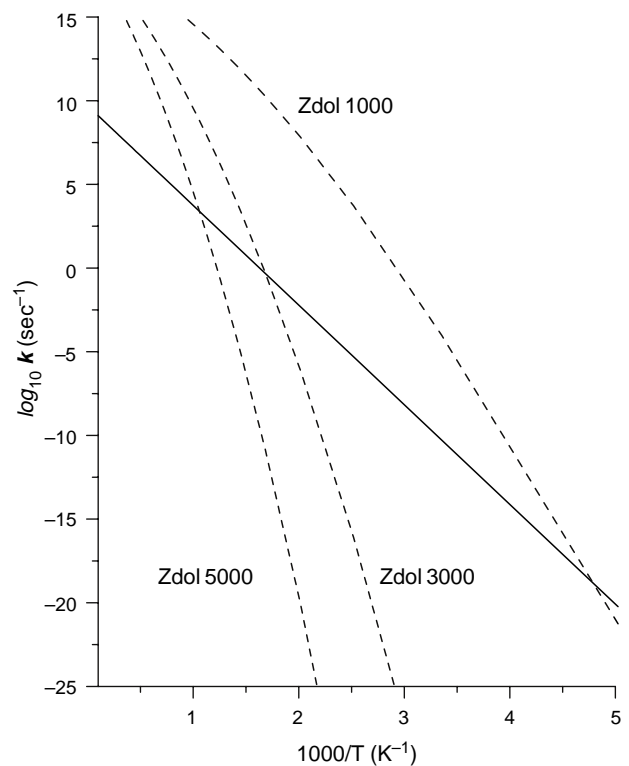


Fig. 4. The relation $\log_{10}(k)$ vs $1/T$ is shown for desorption (dashed line) and decomposition (solid line) of Fomblin Zdol 1000, 3000, and 5000 from carbon surfaces. The crossover temperatures increase with increasing chain length.

behavior and thus $\log(k)$ vs $1/T$ is a straight line. The desorption kinetics for the flexible chain clearly exhibit non-Arrhenius behavior. For comparison purposes we have also included a plot of the desorption rate constant that one would predict if the Fomblin Zdol were a rigid chain. In essence this uses a single value of $\Delta E_{\text{des}}^{\ddagger} = 164$ kJ/mol, the value that one would observe at $T = 0$ K. The important point to note is that at all temperatures chain flexibility effectively lowers the apparent desorption barrier and increases the desorption kinetics above what one would predict for the rigid Fomblin oligomer. The second point to note is that there is a crossover temperature, $T_c = 209$ K (for the flexible Fomblin oligomer) at which the rate constant for desorption is equal to the rate constant for decomposition. In other words for temperatures below 209 K decomposition is the preferred reaction path for Fomblin Zdol 1000 while at higher temperatures the preferred reaction path is desorption. Thus during rapid laser heating of Fomblin Zdol 1000 to temperatures above 209 K one would expect desorption to be the dominant path for lubricant degradation.

Desorption and decomposition reaction kinetics have been compared for Fomblin Zdols with molecular weights in the range 1000–5000 amu. The rate constants are compared in Fig. 4 in the form $\log(k)$ vs $1/T$ for Fomblin Zdol 1000, 3000 and 5000. The desorption rate constants for all the Fomblin Zdols exhibit non-Arrhenius behavior. This originates from the temperature dependence of $\Delta E_{\text{des}}^{\ddagger}$.

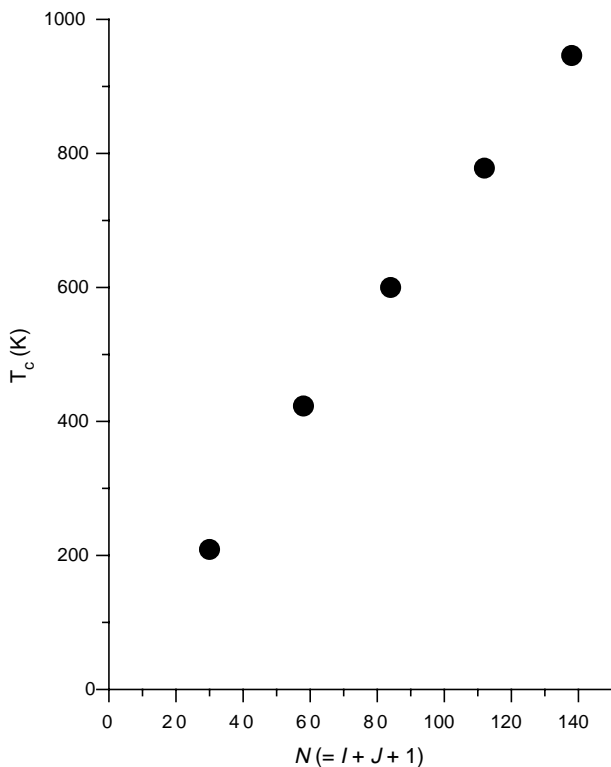


Fig. 5. The crossover temperature for the desorption and decomposition rate constants as a function of chain length. The crossover temperature is almost linear in the chain length.

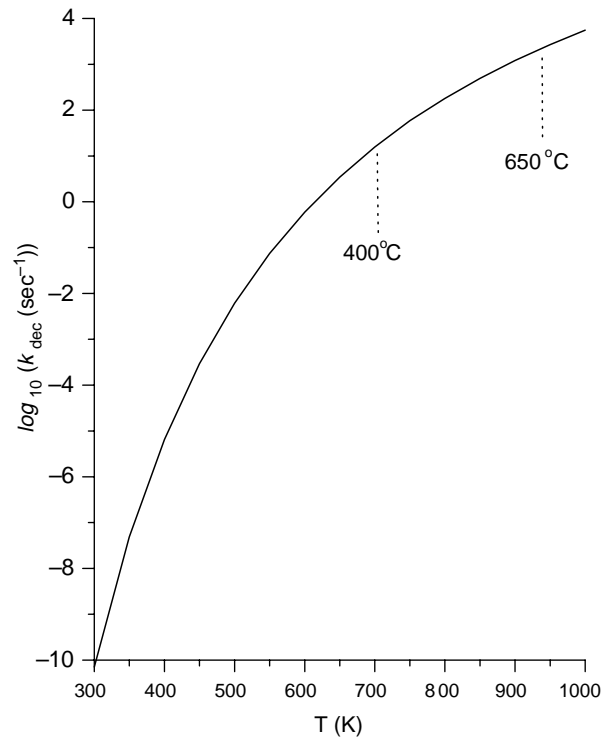


Fig. 6. The rate constant for Fomblin Zdol decomposition, $\log_{10}(k_{\text{dec}})$, vs temperature. The rate constant is insignificant at 300 K but is significant in the temperature range anticipated for use in HAMR applications.

Increasing the surface temperature increases the configurational entropy of molecules on the surface and decreases the magnitude of the effective $\Delta E_{\text{des}}^{\ddagger}$. The crossover temperatures, T_c , increase with molecular weight and are plotted as a function of chain length in Fig. 5. These results indicate that Fomblin Zdols with molecular weight up to 3000 are most likely to desorb from the surface during laser induced annealing to 400 °C (or 673 K) while Fomblin Zdols with molecular weights above 4000 are most likely to decompose on the surface. For rapid laser heating to temperatures of 650 °C (or 920 K) the Fomblin Zdols with molecular weights up to 4000 amu are likely to desorb while those with molecular weights higher than 5000 are most likely to decompose.

Although the decomposition kinetics do not depend on chain length they do depend on temperature. Fig. 6 plots the decomposition rate constant in the temperature range from 300 to 1000 K. Although the decomposition rate constant is insignificant at room temperature it does become significant at the temperatures anticipated for use with HAMR. Under the conditions that one would expect to be used for HAMR the highest molecular weight fractions of Fomblin Zdol lubricants are likely to remain on the disk surface but may be subject to decomposition as a result of heating. It is important to keep in mind, of course, that decomposition is likely to result in the formation of short PFPE oligomers that are then prone to desorption during further heating.

6. Conclusion

Analysis of the decomposition and desorption kinetics of Fomblin Zdol lubricants on the carbon overcoats used for magnetic recording applications indicates that under HAMR conditions the low molecular weight fractions (< 3000 amu) are most likely to desorb during laser heating while the higher molecular weight fractions are likely to decompose. Thus, the lifetime of the high molecular weight fractions of the lubricant is dictated by their decomposition kinetics.

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