

Conformational Entropy Effects on the Desorption Kinetics of Polyethers from Graphite

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The desorption kinetics of a series of poly(ethylene glycol)-dimethyl ethers (PEG-DMEs, $\text{CH}_3(\text{OCH}_2\text{-CH}_2)_n\text{OCH}_3$, $n = 1-22$) adsorbed on graphite have been measured to study the detachment of flexible linear heteropolymers from solid surfaces. Desorption rates were measured using temperature programmed desorption (TPD) and indicate that the desorption of the PEG-DMEs from graphite can be described using a first-order rate constant and a desorption barrier, $\Delta E_{\text{des}}^\ddagger$, that is independent of adsorbate coverage. The average pre-exponent of the first-order desorption rate constant was measured to be $\nu_{\text{av}} = 10^{18.8 \pm 0.7} \text{ s}^{-1}$ and is roughly independent of the PEG-DME oligomer chain length. In addition the $\Delta E_{\text{des}}^\ddagger$ scales nonlinearly with the oligomer chain length and can be represented by the expression $\Delta E_{\text{des}}^\ddagger = a + bN^\gamma$ (where $N = 3n + 3$), with the exponent assuming a value of $\gamma = 0.46 \pm 0.01$. A simple theory generates an analytical expression for the measured values of $\Delta E_{\text{des}}^\ddagger$ that accurately reproduces the measured nonlinearity of $\Delta E_{\text{des}}^\ddagger(N)$. The measured value of $\Delta E_{\text{des}}^\ddagger$ is determined by the difference in the average energy of the adsorbed state, $\langle E \rangle$, and the average energy of the transition state to desorption, $\langle E^\ddagger \rangle$. The nonlinear dependence of the $\Delta E_{\text{des}}^\ddagger$ on chain length can be ascribed to conformational entropy in the adsorbed state. For long oligomers entropy favors conformations of the molecule that are partially detached from the surface at elevated temperatures and thus the average energy of the adsorbed state is quite different from that of the minimum energy configuration.

1. Introduction

The statics and dynamics of macromolecules adsorbed on solid surfaces are of both theoretical and practical interest because polymeric films are capable of modifying interfacial properties in a controlled manner. The growing interest in polymer adsorption onto solid substrates is due to their critical role in numerous industrial and biological applications such as stabilization of colloidal suspensions, paints and coatings, biomaterial compatibility, and lubricant coatings on magnetic recording disks. The function of thin polymeric films is intriguing because these films represent examples of two-dimensional matter that can exhibit physical and dynamic properties that are dramatically different from their bulk phase properties. In addition, the behavior of adsorbed macromolecules can be much different from that of small adsorbates on surfaces. The most notable factor contributing to the differences in the behavior of adsorbed macromolecules and that of small molecules is the large number of configurations that macromolecules can adopt at an interface. As a result, intense research efforts have focused on understanding the statics of adsorbed polymers and the effects of molecular conformation on basic properties such as film thickness, coverage, and segment density distribution in the near-surface region.^{1,2} The results of these studies provide a comprehensive description of adsorbed polymer layers under equilibrium conditions.

Although the equilibrium properties of polymers at surfaces have been studied extensively, in many cases

adsorbed polymer layers do not reach an equilibrium state. The dynamics of macromolecules under nonequilibrium conditions are just as important as their equilibrium properties but have been much less thoroughly studied. This is especially surprising because the morphologies of adsorbed polymer materials are often governed by kinetic rather than equilibrium parameters.³ For example, the kinetics of order–disorder transitions within adsorbed polymer films have a significant impact on phenomena such as polymer evaporation or desorption from surfaces. This is important in determining the rate of evaporative loss of lubricants from the surfaces of magnetic storage media, a process that generally leads to a substantial decrease in wear durability. As another example, oligomer desorption from catalyst surfaces represents the final step in the Fischer–Tropsch synthesis of high molecular weight hydrocarbons. All of these represent examples of oligomer or polymer desorption processes from surfaces.

The vast majority of measurements of molecular desorption kinetics from surfaces have used relatively small species for which the desorption process is considered simply as a displacement along the surface normal. This desorption mechanism can be adequately modeled using a single well-defined reaction coordinate for motion over a simple one-dimensional potential energy surface describing the interaction of the molecule with the surface. In many such studies of series of homologous compounds the energy barriers to desorption, $\Delta E_{\text{des}}^\ddagger$, have been found to scale linearly with the chain length. For example, the desorption of *n*-alkanes ($N = 6-12$) from the Au(111) surface was studied by Wetterer et al. using helium atom

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reflectivity.⁴ Their conclusions from that study indicate that the desorption energies, $\Delta E_{\text{des}}^{\ddagger}(N)$, increased incrementally by 6.2 ± 0.2 kJ/mol per methylene unit. A recent study by Bishop et al. has reported segment–surface interaction energies of ~ 8 kJ/mol per methylene group for *n*-alkanes ($N = 6–10$) adsorbed on Pt(111).⁵ This was the first study to suggest that the $\Delta E_{\text{des}}^{\ddagger}(N)$ might not be truly linear in chain length, but the limited range of the chain lengths used makes it difficult to determine the functional form of this nonlinearity. Needless to say, it is not surprising that over the limited range of chain lengths used in all such studies, $\Delta E_{\text{des}}^{\ddagger}(N)$ would appear to be linear in chain length.

In contrast with the desorption of small molecules, the description of the desorption of a long flexible molecule from a surface must take into consideration the fact that the molecular structure has many degrees of freedom that provide many energetically equivalent pathways leading to desorption. The combined contributions of these pathways must influence the overall desorption reaction kinetics and the $\Delta E_{\text{des}}^{\ddagger}$ that one measures for such species. In a previous report we presented the results of a study of the desorption of *n*-alkanes ($\text{C}_N\text{H}_{2N+2}$) from graphite that was the first to use a set of oligomer chain lengths, $N = 5–60$, broad enough to allow observation of a *nonlinear* dependence of $\Delta E_{\text{des}}^{\ddagger}$ on N .^{6–8} In fact, $\Delta E_{\text{des}}^{\ddagger}$ was found to obey an offset power law of the form $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$ where the exponent had a value of $\gamma = 0.50 \pm 0.01$. In addition, we were able to propose a mechanism for the desorption process and a model for the energy and the entropy of the oligomers on the surface. The model yields an analytical expression for the measured values of $\Delta E_{\text{des}}^{\ddagger}(N)$ that provides an extremely good quantitative fit to the data. Those results revealed that the nonlinear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on N can be attributed to the conformational isomerism or conformational entropy of the adsorbed oligomer that causes some fraction of the chain segments to be detached from the surface at any temperature above absolute zero.

On the basis of the model proposed for the desorption of *n*-alkane oligomers from graphite, it can be reasoned that the desorption kinetics of similar long chain molecules might be influenced by conformational entropy in the adsorbed state and thereby show a nonlinear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on chain length. We have chosen to investigate this possibility by measuring the desorption kinetics for a set of seven poly(ethylene glycol) dimethyl ether oligomers [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, $n = 1$ to ~ 22] from graphite. These molecules will be referred to in this paper as PEG-DMEs. Desorption rates were measured using temperature-programmed desorption (TPD) and indicate that desorption of the PEG-DMEs can be described using a first-order rate constant and a $\Delta E_{\text{des}}^{\ddagger}$ that is independent of coverage. The average value of the pre-exponent of the first-order rate constant was measured to be $v_{\text{av}} = 10^{18.8 \pm 0.7}$

s^{-1} and is roughly independent of the PEG-DME oligomer chain length. As in the case of the *n*-alkanes, the values of $\Delta E_{\text{des}}^{\ddagger}$ scale nonlinearly with the oligomer chain length and can be represented by the expression $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$ (where $N = 3n + 3$) with the exponent having a value of $\gamma = 0.46 \pm 0.01$. As in the case of the alkanes we have proposed a mechanism for the desorption process and a model that accounts for the energy and entropy of the adsorbed PEG-DME oligomers. This model generalizes that for the alkanes to heteropolymers with more than one type of backbone bond. Once again this yields an analytical expression for the measured values of $\Delta E_{\text{des}}^{\ddagger}$ that provides an extremely accurate, quantitative fit to the observed nonlinear chain length dependence of $\Delta E_{\text{des}}^{\ddagger}$. The model explicitly accounts for contributions to the free energy of the two distinct types of chemical segments that form the PEG-DME backbone (the C–C and O–C bonds). The results of our modeling of PEG-DME desorption confirm our previous suggestion that conformational entropy plays a significant role in determining the desorption kinetics of oligomers from surfaces and suggests that the desorption of all such flexible linear oligomers occurs through a common mechanism.

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. TPD experiments were performed using an ABB Extrel Merlin quadrupole mass spectrometer (QMS). 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.

The substrate used was a $12 \times 12 \times 2$ 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 that was ~ 0.25 mm thick using electrically conductive silver epoxy purchased from the 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.

A set of monodisperse PEG-DMEs ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, $n = 1–4$) were purchased in purities of $>99.0\%$ from Fluka Chemicals. Relatively monodisperse PEG-DMEs ($n \approx 8, 10, 22$) each having polydispersity <1.08 were also purchased from Fluka Chemicals. Although the PEG-DME samples were all nominally monodisperse, the species with $n \geq 8$ required extensive distilling prior to use to remove low molecular weight precursors used in their synthesis. This purification procedure consisted of heating the PEG-DME samples in a glass vial under vacuum for ~ 12 h at temperatures ranging from 333 K for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_8\text{OCH}_3$ to 413 K for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{22}\text{OCH}_3$. The purities of the compounds were further verified by measuring the heats of vaporization directly from multilayer desorption peaks generated in their TPD spectra and comparing these measured values of the heats of vaporization with values reported in the literature. These data will be presented in later sections of this paper. The PEG-DMEs with $n = 1$ and 2 were introduced into the vacuum chamber through leak valves. Deposition of the PEG-DMEs with $n \geq 3$ was performed with a high molecular weight doser. For the species with $n = 3$ and 4 the bulk phase was maintained at room temperature in the glass vial of the doser. The deposition temperatures of the bulk PEG-DMEs with $n \geq 8$ were chosen to be the same as those used for their purification. On the basis of

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a report by Calahorra et al. indicating a bulk decomposition temperature of 623 K for the PEG-DMEs, no decomposition is expected at the distillation or deposition temperatures chosen.⁹

Prior to each set of TPD experiments conducted with a given PEG-DME, 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 on the basis of observations made in previous studies.^{10,11} In addition, the desorption spectra were highly reproducible, indicating that no contamination of the surface occurred as a result of any adsorbate decomposition. The desorption peaks for submonolayer coverages of heptane (C₇H₁₆) were used to assess the reproducible nature of the surface and the TPD spectra. During a normal TPD experiment using heptane the desorption temperature was consistently found to be 211 K and the width of the desorption peak at half-maximum was <7 K. The width of the desorption peak for heptane was also used as a basis for assessing the uniformity of the surface temperature during heating.

The feature of our apparatus that allowed experiments with long chain PEG-DMEs ($n \geq 3$) is a dosing system developed to allow the introduction of species with extremely low vapor pressures. This device has been described in detail in a previous paper but basically consists of a heated zone in which the species of interest is vaporized and a long collimating tube which can be positioned directly in front of the graphite sample or directly in front of the aperture to the mass spectrometer.⁷ The vapor of the adsorbate travels from the glass vial down the length of the collimating tube and is deposited onto the substrate which is held at ~120 K.

Within the UHV chamber the graphite substrate was positioned to face either the stainless steel dosing tube from the leak valve or the stainless steel dosing tube from the high mass deposition source. TPD studies were performed by cooling the graphite sample in UHV to ~120 K and exposing its surface to vapor of the PEG-DMEs. Following adsorption of the PEG-DMEs on 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 temperature necessary to induce the desorption of all adsorbed species. During heating, the QMS was used to monitor the desorption rate of the adsorbed PEG-DMEs and any decomposition products, if present. In all cases, adsorption of the PEG-DMEs was both molecular and reversible with no indication of decomposition during desorption.

3. Results

The rate of a first-order desorption process from a surface is expressed as

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

where r is the desorption rate, θ is the fractional coverage of the adsorbed species, k_{des} is the desorption rate constant, ν is a preexponential factor for desorption, $\Delta E_{\text{des}}^{\ddagger}$ is the desorption barrier, k_{B} is Boltzmann's constant, and T is temperature. The following sections describe the determination of the values of ν and $\Delta E_{\text{des}}^{\ddagger}$ for the PEG-DMEs in the length range CH₃OCH₂CH₂OCH₃ to CH₃(OCH₂CH₂)₂₂OCH₃ adsorbed on graphite.

3.1. Evaluation of Reaction Order for PEG-DME Desorption from Graphite. Prior to any detailed analysis of the kinetics of PEG-DME desorption, it is necessary to ascertain that the desorption process is indeed

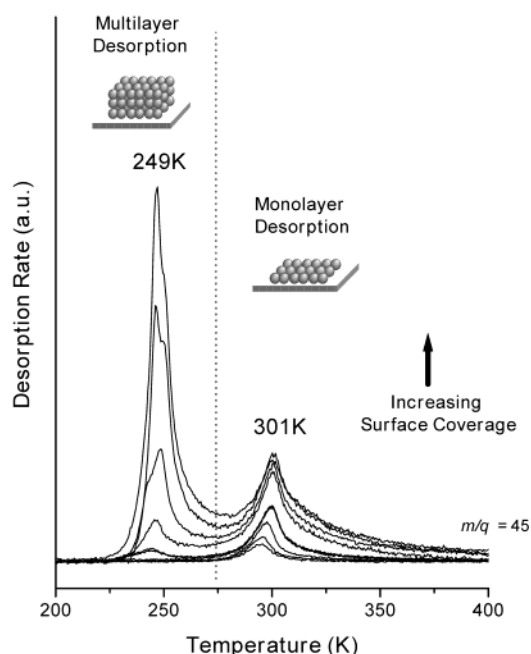


Figure 1. TPD spectra of CH₃(OCH₂CH₂)₄OCH₃ adsorbed at various coverages on the graphite surface at 120 K. The desorption peak at ~300 K is assigned to desorption of the CH₃(OCH₂CH₂)₄OCH₃ monolayer. The desorption features at ~249 K are assigned to desorption of CH₃(OCH₂CH₂)₄OCH₃ multilayers. The monolayer desorption temperature is 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 $m/q = 45$ (C₂H₅O⁺). The heating rate was 2 K/s.

first-order and describable by eq 1. The order of the desorption reaction of the PEG-DMEs on graphite has been determined by performing TPD experiments using a constant heating rate of $\beta = 2$ K/s and initial PEG-DME coverages varying from submonolayer to many multilayers. Figure 1 shows the TPD spectra of CH₃(OCH₂CH₂)₄OCH₃ for different initial coverages adsorbed on the graphite surface at 120 K. Deposition of CH₃(OCH₂CH₂)₄OCH₃ was performed with the bulk phase in the high molecular weight doser maintained at room temperature. The TPD spectra were generated by using the QMS to monitor the signal at $m/q = 45$ (C₂H₅O⁺) during heating. Several additional mass-to-charge ratios including $m/q = 59$ (C₃H₇O⁺), $m/q = 73$ (C₄H₉O⁺), and $m/q = 87$ (C₅H₁₁O⁺) were monitored to detect the desorption of any decomposition products, if present. The desorption signals at these m/q ratios all occurred at the same temperatures suggesting that they are all due to desorption of the same molecule and that there is no decomposition of the CH₃(OCH₂CH₂)₄OCH₃ on graphite during heating. No decomposition of any of the PEG-DMEs studied was observed during heating on the graphite surface.

At the lowest coverage, CH₃(OCH₂CH₂)₄OCH₃ desorbs over a relatively narrow temperature range and achieves a maximum rate of desorption at 295 K, as shown in Figure 1. As the PEG-DME exposure to the surface is increased, the desorption peak increases in intensity and shifts to ~300 K. As the exposure is increased further, the monolayer saturates and a second desorption feature grows in at ~249 K, which indicates the onset of multilayer desorption. This low-temperature desorption feature continues to grow with increasing coverage and displays zero-order kinetics in that the leading edges of these peaks overlap one another at the highest coverages.

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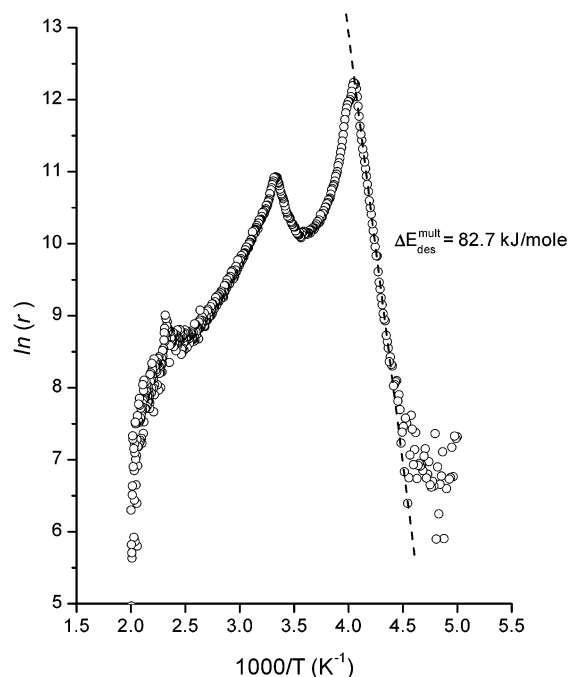


Figure 2. Arrhenius representation of the TPD spectrum for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ measured at the highest coverage. A line has been fit to the leading edge of the multilayer desorption feature, and its slope is a measure of the $\Delta E_{\text{des}}^{\text{mult}}$ for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$.

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 PEG-DMEs. This analysis has been especially important for evaluating the purities of those PEG-DMEs that were supplied in polydisperse form. The desorption energy for the multilayer, $\Delta E_{\text{des}}^{\text{mult}}$, has been determined using the fact that the leading edge of the multilayer desorption peak exhibits zero-order desorption kinetics and, therefore, that the following expression can be used to determine $\Delta E_{\text{des}}^{\text{mult}}$ from the desorption rate measured over the low-temperature side of the multilayer desorption peak.

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

The values of the $\Delta E_{\text{des}}^{\text{mult}}$ of the PEG-DMEs should be close to their heats of bulk vaporization, ΔH_{vap} . The data for the desorption of the $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ multilayer are presented in Figure 2 and reveal that the $\Delta E_{\text{des}}^{\text{mult}}$ of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ is 82.7 ± 1.8 kJ/mol. This is consistent with the ΔH_{vap} of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ reported by Nichols et al. from a series of correlation gas chromatography (GC) measurements on numerous polyethers and crown ethers.¹² The GC retention times of the various species studied were used to correlate their ΔH_{vap} with those of a series of standard compounds. The ΔH_{vap} of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ reported by Nichols et al. was 76.9 ± 2.6 kJ/mol and is similar in magnitude to the value of $\Delta E_{\text{des}}^{\text{mult}}$ determined from our measurements.

The agreement between the value of $\Delta E_{\text{des}}^{\text{mult}}$ found for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ in this work and the value of ΔH_{vap} reported in the literature indicates that the purified sample of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ is free of any low mass

Table 1. Multilayer Peak Desorption Temperatures for the PEG-DMEs and Their Corresponding Desorption Energies, $\Delta E_{\text{des}}^{\text{mult}}$ ^a

ethylene oxide units, <i>n</i>	$T_{\text{p}}^{\text{mult}}$ (K)	measured $\Delta E_{\text{des}}^{\text{mult}}$ (kJ/mol)	ΔH_{vap} (kJ/mol)
1	146	37.6 ± 1.0	36.8 ± 0.2^b
2	187	49.8 ± 1.3	48.0 ± 0.6^c
3	223	62.9 ± 2.0	63.7 ± 3.3^c
4	251	82.7 ± 1.8	76.9 ± 2.6^c
~8	339	134.5 ± 3.3	131.2^d
~10	386	163.8 ± 5.5	162.5^d
~22	ND ^e	ND ^e	317.5^d

^a The purity of the PEG-DMEs has been ascertained by comparing the measured values of $\Delta E_{\text{des}}^{\text{mult}}$ with the ΔH_{vap} reported in the literature. ^b Reference 10. ^c Reference 11. ^d Estimates based on a linear extrapolation of the literature data for PEG-DMEs with $n \leq 4$. ^e ND = not determined.

contaminants and that the species exiting the dosing tube is the molecule of choice (i.e., of the reported M_n). Using a similar procedure, the $\Delta E_{\text{des}}^{\text{mult}}$ of each PEG-DME used was evaluated and compared with values of ΔH_{vap} reported in the literature. Table 1 summarizes the multilayer desorption temperatures observed for the PEG-DMEs as well as the $\Delta E_{\text{des}}^{\text{mult}}$ determined in this study and the ΔH_{vap} reported in the literature. The $\Delta E_{\text{des}}^{\text{mult}}$ of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{22}\text{OCH}_3$ was not determined because the exposures needed to generate multilayer films on graphite were too high. The agreement between the values of $\Delta E_{\text{des}}^{\text{mult}}$ and the reported values of ΔH_{vap} is very good and indicates that the desorption experiments have been performed with very highly monodisperse samples of the desired molecular weight.

For all of the PEG-DMEs studied the dependence of the desorption spectra on coverage is similar to that shown for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ in Figure 1. Both the monolayer and multilayer peak desorption temperatures, T_{p} , increase as the number of monomer units, n , in the backbone increases. Figure 3 illustrates the TPD spectra measured for each of the PEG-DMEs for an initial coverage of roughly one monolayer. In all cases the desorption temperature of the PEG-DME coverage, indicating that the desorption process is first-order and that there is little coverage dependence on the desorption barrier, $\Delta E_{\text{des}}^{\ddagger}$. The shift of T_{p} with coverage in the submonolayer regime varied from a minimum of 2 K for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{22}\text{OCH}_3$ to a maximum of 8 K for $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$. The small variation of the T_{p} of the PEG-DMEs with coverage indicates that there is very little coverage dependent interaction between the adsorbed molecules. The interactions that are observed are not significant enough to justify an analysis other than the use of a simple first-order rate expression, as written in eq 1. This is consistent with the analysis of the kinetics of the desorption of poly(ethylene glycol) oligomers ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, $n = 1$ to ~13) from a silica surface, as reported by Handschuh et al.¹³ Similar first-order coverage-independent desorption kinetics were also observed in our prior study of the desorption of n -alkanes from graphite.^{6,7} On the basis of our observations and those reported by Handschuh et al., it is reasonable to suggest that the PEG-DMEs desorb from the graphite surface with first-order, coverage independent kinetics.

3.2. Measurement of $\Delta E_{\text{des}}^{\ddagger}$ and ν for PEG-DMEs from Graphite. TPD experiments performed with a

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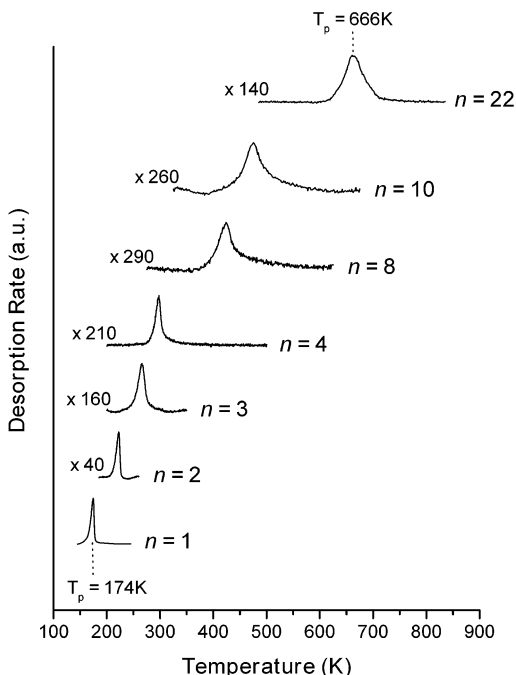


Figure 3. TPD spectra of the PEG-DMEs with $n = 1$ to ~ 22 following adsorption of approximately one monolayer on the graphite surface at 120 K. Both the desorption peak temperature and peak width increase with increasing chain length. All spectra were generated using a mass spectrometer to monitor the signal at $m/q = 45$ ($C_2H_5O^+$) during heating. The heating rate was 2 K/s in all cases.

constant heating rate and variable coverages of PEG-DMEs on graphite have shown that the desorption kinetics of this system may be represented by a simple first-order rate expression. As a first approximation, the preexponential factor, ν , shown in eq 1 is often assumed to have a value of $k_B T/h \approx 10^{13} \text{ s}^{-1}$, as suggested by conventional transition state theory.¹⁴ A more thorough and accurate analysis of the desorption kinetics of the PEG-DMEs, however, requires that the preexponential factors be determined experimentally. We have therefore measured both ν and $\Delta E_{\text{des}}^\ddagger$ independently for the PEG-DMEs in an effort to accurately interpret their desorption kinetics from graphite. TPD spectra were recorded for the PEG-DMEs 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 to 5 K/s. Figure 4 illustrates the variable heating rate TPD spectra for $CH_3(OCH_2CH_2)_4OCH_3$ measured using the QMS to monitor the signal at $m/q = 45$ ($C_2H_5O^+$). The $CH_3(OCH_2CH_2)_4OCH_3$ monolayer desorbed with a maximum rate from the graphite surface at $T_p = 286$ K when the graphite surface was heated at a rate of $\beta = 0.2$ K/s. As the heating rate was increased in subsequent experiments, the desorption peaks increased in intensity and shifted to higher temperatures. TPD experiments using a heating rate of $\beta = 5$ K/s induced desorption of the $CH_3(OCH_2CH_2)_4OCH_3$ monolayer at $T_p = 306$ K.

Analysis of the heating rate dependence of the peak desorption temperature can be used to determine ν and $\Delta E_{\text{des}}^\ddagger$ independently. Shown in the inset to Figure 4 is a plot of $\ln(\beta/T_p^2)$ vs $1/T_p$, where T_p is dependent on the heating rate, β . For a first-order desorption process TPD data presented in the form $\ln(\beta/T_p^2)$ vs $1/T_p$ should yield a line with a slope equal to $-\Delta E_{\text{des}}^\ddagger/k_B$.¹⁵ A linear regres-

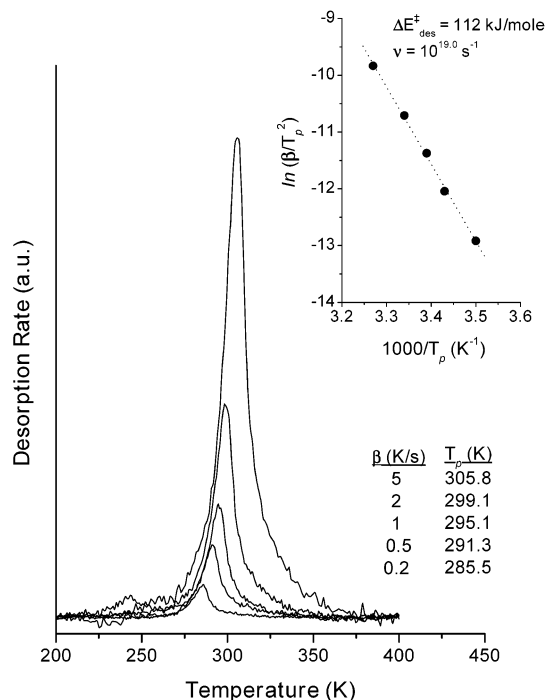


Figure 4. TPD spectra of $CH_3(OCH_2CH_2)_4OCH_3$ measured at varying heating rates (β) for initial coverages of approximately one monolayer. Heating rates varying from 0.1 to 5 K/s were used to desorb the $CH_3(OCH_2CH_2)_4OCH_3$ monolayer. The monolayer desorption temperatures increase with increasing heating rate. The spectra were generated using a mass spectrometer to monitor the signal at $m/q = 45$ ($C_2H_5O^+$) during heating. The inset is a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the desorption of $CH_3(OCH_2CH_2)_4OCH_3$ from the graphite surface. The slope of the linear fit has been used to estimate the $\Delta E_{\text{des}}^\ddagger$ for $CH_3(OCH_2CH_2)_4OCH_3$ from graphite.

sion performed on the data in the inset of Figure 4 indicates that $\Delta E_{\text{des}}^\ddagger = 111.9 \pm 2.8$ kJ/mol for $CH_3(OCH_2CH_2)_4OCH_3$. Figure 4 and its inset qualitatively illustrate the desorption behavior for all the PEG-DMEs studied using variable heating rate TPD experiments. Values of $\Delta E_{\text{des}}^\ddagger$ for the full set of PEG-DMEs studied using variable heating rate TPD experiments were calculated in a manner similar to that used for $CH_3(OCH_2CH_2)_4OCH_3$.

With the $\Delta E_{\text{des}}^\ddagger$ of the PEG-DMEs measured, it is possible to evaluate the preexponential factors for desorption for each PEG-DME studied using variable heating rate TPD experiments. The preexponential factors for desorption, ν , may be estimated using Redhead's equation for first-order kinetics

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

where T_p depends on the heating rate, β .¹⁵ As indicated by eq 3, a preexponential factor for desorption may be calculated at each heating rate. Figure 5 illustrates the averaged preexponential factors as a function of the number of monomer units, n , for each PEG-DME studied. Note that the y -axis displays $\log(\nu)$ and that the preexponential factors for desorption of the PEG-DMEs from graphite assume values in the range 10^{18} – 10^{19} s^{-1} as opposed to the value of 10^{13} s^{-1} that is commonly assumed in analysis of TPD spectra. In addition, the value of ν is roughly independent of the chain length with an average

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(15) Redhead, P. A. Thermal Desorption of Gases. *Vacuum* **1962**, *12*, 203–211.

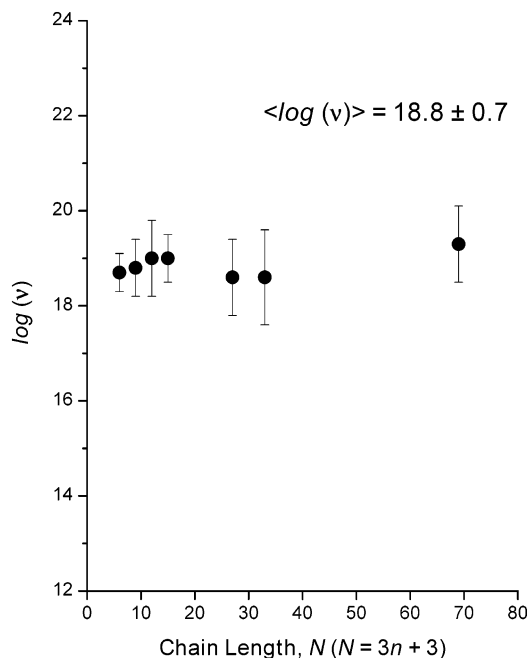


Figure 5. Preexponential factors, ν , of the first-order desorption rate constants, k_{des} , for the PEG-DMEs as a function of the number of ethoxy units, n , in the oligomer ($n = 1$ to ~ 22). The values of ν were calculated using a Redhead analysis from the TPD spectra measured at varying heating rates ($\beta = 0.1$ – 5 K/s). The preexponential factors range from 10^{18} to 10^{19} s^{-1} . The value of $\log(\nu)$ is nearly independent of chain length with an average value of $\nu_{\text{av}} = 10^{18.8 \pm 0.7} \text{ s}^{-1}$.

Table 2. Desorption Barriers, $\Delta E_{\text{des}}^{\ddagger}$, and the Pre-exponential Factors, ν , of the PEG-DMEs Measured from a Redhead Analysis of Variable Heating Rate TPD Data

ethylene oxide units, n	$\log(\nu)$	$\Delta E_{\text{des}}^{\ddagger}$ (kJ/mol)
1	18.7 ± 0.4	64.0 ± 1.5
2	18.8 ± 0.6	82.7 ± 2.6
3	19.0 ± 0.8	98.4 ± 4.1
4	19.0 ± 0.5	111.9 ± 2.8
~ 8	18.6 ± 0.8	157.5 ± 6.3
~ 10	18.6 ± 1.0	177.3 ± 9.4
~ 22	19.3 ± 0.8	254.8 ± 10.0

value of $\nu_{\text{av}} = 10^{18.8 \pm 0.7} \text{ s}^{-1}$. Table 2 lists the values of $\Delta E_{\text{des}}^{\ddagger}$ and ν for all of the PEG-DMEs used in this study.

The desorption pre-exponents measured for the PEG-DMEs are all quite high and independent of chain length. This suggests that the high value of ν is due to a degree of freedom common to all the PEG-DMEs such as center of mass translation in the transition state. Both the high value of the desorption pre-exponent and its independence of chain length have also been observed in our prior work on n -alkane desorption from graphite.^{6,7} The pre-exponents of a set of nine n -alkanes ($\text{C}_N\text{H}_{2N+2}$) having chain lengths in the range $N = 7$ – 44 were measured and found to have an average value of $\nu_{\text{av}} = 10^{19.6 \pm 0.5} \text{ s}^{-1}$ that was roughly independent of chain length. The independence of the desorption pre-exponent on chain length has also been reported in the study by Handschuh et al. of poly(ethylene glycol) oligomers desorbing from a silica surface.¹³ The preexponential factors for desorption of poly(ethylene glycol) oligomers with $n \leq 13$ were found to be independent of chain length with an average value on the order of $\nu_{\text{av}} = 10^{16.3} \text{ s}^{-1}$. The relatively high values of the desorption pre-exponents seem to be a common feature of oligomer desorption from surfaces.

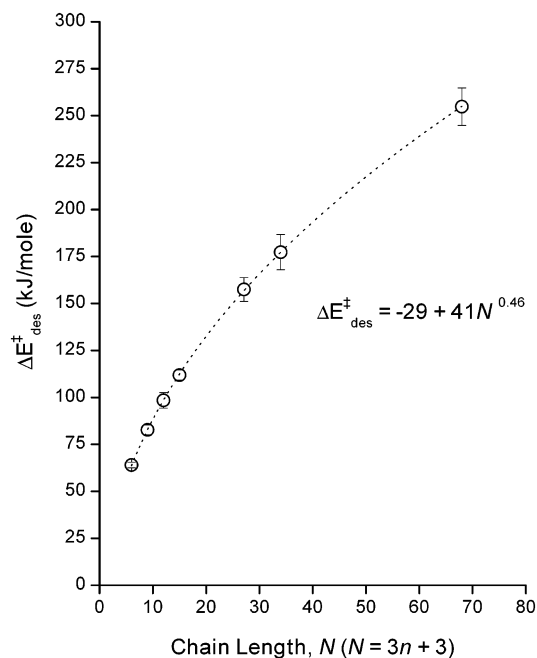


Figure 6. Desorption barriers, $\Delta E_{\text{des}}^{\ddagger}$, of the PEG-DMEs from graphite as a function of chain length, N , where $N = 3n + 3$. The desorption barriers reported have been calculated using a Redhead analysis of the TPD data measured at variable heating rates ranging from 0.1 to 5 K/s for an initial coverage of one monolayer in each case. These data clearly indicate that the desorption barrier is nonlinear in the PEG-DME oligomer chain length. The dashed line is a fit of the data to a power-law of the form $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$, with the parameters taking values of $a = -29 \pm 3$ kJ/mol, $b = 41 \pm 2$, and an exponent of $\gamma = 0.46 \pm 0.01$.

3.3. Chain Length Dependence of $\Delta E_{\text{des}}^{\ddagger}$. The $\Delta E_{\text{des}}^{\ddagger}$ of the PEG-DMEs have been determined by conducting TPD studies using heating rates ranging from 0.2 to 5 K/s for constant initial PEG-DME coverages of approximately one monolayer. As in our previous work with the n -alkanes on graphite, we chose to investigate the effects of chain length on the $\Delta E_{\text{des}}^{\ddagger}$ to evaluate the effects of conformational entropy on the desorption kinetics of the PEG-DMEs. The chain length of the PEG-DMEs will be denoted by N , where $N = 3n + 3$ and corresponds to the number of atoms in the oligomer backbone. The chain lengths explored in this work range from $N = 6$ for $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ to $N = 69$ for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{22}\text{OCH}_3$. The rationale for choosing to represent the data in this manner for the PEG-DMEs is that it allows a comparison of the chain length dependence of $\Delta E_{\text{des}}^{\ddagger}$ with that observed for n -alkanes over a similar range of chain lengths ($N = 5$ – 60). Figure 6 illustrates the $\Delta E_{\text{des}}^{\ddagger}$ of the PEG-DMEs from graphite as a function of the chain length, N , and clearly shows that the relationship between the two is nonlinear over the range of chain lengths explored in this work. As a first approach to the analysis of the nonlinear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on N we have fit the data to an offset power law expression of the form $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$. The fitting parameters found for the $\Delta E_{\text{des}}^{\ddagger}$ dependence on chain length are $a = -29 \pm 4$ kJ/mol, $b = 41 \pm 2$, and the exponent is $\gamma = 0.46 \pm 0.01$. The fit of the expression $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$ to the data is shown as the dotted line in Figure 6 and reproduces the data extremely well.

Prior study of the desorption kinetics of the alkanes from the surface of graphite have shown that the dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length can also be

described using the empirical form $\Delta E_{\text{des}}^{\ddagger} = a + bN^{\gamma}$. It is particularly interesting to place the values of the fitting parameters for the PEG-DMEs in context with those previously reported for the desorption of *n*-alkanes from graphite. The fitting parameters found for the alkanes were $a = -29 \pm 4$ kJ/mol and $b = 42 \pm 2$ with an exponent of $\gamma = 0.50 \pm 0.01$.⁷ What is intriguing is that the parameters used to describe the nonlinear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length for both the PEG-DMEs and the *n*-alkanes are remarkably similar in magnitude. The fact that the same functional form is observed for both molecules suggests that the desorption kinetics of these molecules and other molecules with similar linear structures can be described through a common mechanism. The fact that the $\Delta E_{\text{des}}^{\ddagger}$ and the functional form for their dependence on the chain length are almost identical for the *n*-alkanes and for the PEG-DMEs is probably a consequence of the fact that they interact with the graphite surface through weak van der Waals attractions and that these interactions are apparently quite similar in magnitude.

The fact that $(\Delta E_{\text{des}}^{\ddagger} - a)$ scales as $N^{0.46}$ in the case of the PEG-DMEs is also interesting. It should be noted that a true power law representation of $\log(\Delta E_{\text{des}}^{\ddagger})$ vs $\log(N)$ yields a curve with a slope of 0.57 at $N = 6$ that tends to 0.49 at $N \approx 69$. These observations suggest that as a result of configurational entropy the number of monomers interacting with the surface at the desorption temperature is of the order $\sim N^{1/2}$ rather than N . It should be noted that in addition to our model for the dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on desorption length,^{7,8} the origin of the scaling by a power of $\gamma \approx 1/2$ has been addressed explicitly by Krylov et al.¹⁶ In both models the implication of this nonlinear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on N is that entropy in the adsorbed state plays a significant role in determining the desorption kinetics of oligomers from surfaces by decreasing the net $\Delta E_{\text{des}}^{\ddagger}$ for longer chain molecules.

4. Discussion

The results of our studies of PEG-DME desorption as presented in this paper and *n*-alkane desorption discussed in prior papers show that the measured values of their $\Delta E_{\text{des}}^{\ddagger}$ from graphite scale as $\sim N^{1/2}$ in both cases.⁶⁻⁸ This suggests that the same basic mechanism and physics describe the desorption of both species. In our prior work we have presented a mechanism for the desorption process and a model for the energy and entropy of the *n*-alkanes adsorbed on graphite that accurately accounts for the nonlinear dependence of their $\Delta E_{\text{des}}^{\ddagger}$ on chain length.^{7,8} This model will therefore serve as the basis for describing the nonlinear dependence of the $\Delta E_{\text{des}}^{\ddagger}$ on chain length observed for the PEG-DMEs. Our model equates the segments in the oligomers with their bonds. In the case of the alkanes the segments are the C–C bonds. The obvious difference between the *n*-alkanes and the PEG-DMEs is that the PEG-DMEs are composed of two types of segments: C–C bonds and O–C bonds. A model, therefore, is presented below that takes into account the fact that when considered at this level the PEG-DMEs are heteropolymers and that not all bonds are equally flexible. This model also accounts for the fact that the two segments will have different interactions with the surface.

Our approach toward understanding and describing the nonlinear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on N for PEG-DME

desorption from graphite has been to model the system using transition state theory as the basis for describing the desorption rate constant, k_{des} . Our analysis of the desorption kinetics requires models for both the desorption process and for the interaction energies and entropies of the chains as they adopt different configurations on the surface. The desorption mechanism will be described in section 4.1 and will explicitly account for the interactions of the different types of bonds of the PEG-DMEs with the graphite surface. Section 4.2 describes the energies and entropies of the adsorbed oligomers in the various partially detached configurations that they can adopt on the surface. The desorption mechanism and the oligomer–surface interactions are combined in section 4.3 to derive an analytical expression for the $\Delta E_{\text{des}}^{\ddagger}$ that predicts the observed $\Delta E_{\text{des}}^{\ddagger}(N)$ using the microscopic segment–surface interaction energies as fitting parameters. The comparison of this expression to the data for the desorption kinetics of the PEG-DME oligomers is made in section 4.4.

4.1. Oligomer Desorption Mechanism. The desorption kinetics of small molecules from surfaces are measured and studied routinely using TPD methods. Desorption of small molecules from a surface is usually considered in terms of a fairly simple one-dimensional potential energy surface with a single reaction coordinate that describes the motion of the adsorbate from its adsorbed state into the gas phase. The $\Delta E_{\text{des}}^{\ddagger}$ is the difference in the zero-point energy of the adsorbed species and the energy of a transition state that lies along the reaction coordinate leading from the adsorption well into the vacuum. Although the adsorbate–surface interaction potential for a polyatomic adsorbate has many degrees of freedom in addition to the reaction coordinate for desorption, one generally thinks of these as contributing to the desorption rate constant only through the partition functions for the adsorbed species and for the transition state to desorption. If the adsorbed PEG-DMEs used in this work were thought of as rigid rods and desorption were simply the translation of the center of mass along the surface normal, then this simple description would be adequate. However, such a description of the system would tend to predict that the $\Delta E_{\text{des}}^{\ddagger}$ should be linear in the chain length, N , and that is obviously not the case.

Our previous work with the *n*-alkanes on graphite indicates that their desorption cannot be thought of as simple motion along a single reaction coordinate.⁶⁻⁸ One can imagine an adsorbed oligomer passing through many possible, energetically equivalent configurations on the surface as its structure approaches a number of possible and energetically equivalent transition states to desorption. In essence, there is a multiplicity of energetically equivalent pathways or reaction coordinates along which desorption might occur. This multiplicity of paths certainly must contribute to the measured value of the $\Delta E_{\text{des}}^{\ddagger}$ and therefore must be included within a model for the desorption process.

The poly(ethylene glycol) dimethyl ethers used in this work have the general molecular formula $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, where n has varied from 1 to ~ 22 . The model developed previously for the description of *n*-alkane desorption equates the segments of the oligomer with its bonds; in that case C–C bonds. In this case we consider the PEG-DMEs to consist of $(3n + 2)$ or $(N - 1)$ covalent bonds including $I = n$ C–C bonds and $J = 2n + 2$ C–O bonds. The bonds are equated with the segments of the oligomer. These segments each attach and detach from the surface reversibly and independently. The state of a

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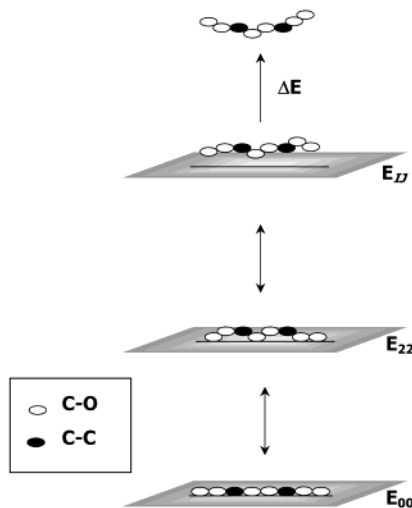


Figure 7. Hypothetical conformations of a PEG-DME oligomer ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$) at different stages of detachment. The oligomer in this case is considered to consist of 8 covalent bonds: $I = 2$ internal C-C bonds and $J = 6$ C-O bonds. The coverages of each of the partially detached oligomers may be described by the number of detached bonds of each type denoted i and j . The fully attached state has $i = j = 0$. The partially detached state has $i = j = 2$. Desorption of the fully detached species ($i = I, j = J$) has a barrier ΔE . The conformations adopted in each of these states are in equilibrium with one another and the relative concentrations of each are related by simple equilibrium constants.

particular PEG-DME oligomer on the surface will be denoted by the number of *detached* bonds, i and j , of each type, C-C and C-O. For example, Figure 7 shows $\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$ in various stages of detachment: fully attached ($i = j = 0$), partially detached ($i = j = 2$), and fully detached. The oligomer coverages in each of these states are given by θ_{ij} and their energies by E_{ij} . Thus there will be a total of $(I + 1)(J + 1)$ states that can be adopted by a partially detached oligomer each with different numbers of detached bonds. Each state can be denoted by different values of i ($= 0$ to I) and j ($= 0$ to J). Our model for the desorption process suggests that there is rapid and reversible attachment and detachment of the oligomer segments to and from the surface. In other words these reversible steps all occur rapidly on the time scale of the net oligomer desorption process. This is a reasonable assumption given that the energy to detach a segment is far less than the net energy required to desorb the entire oligomer. Reattachment of a segment to the surface is rapid because it is probably not activated. The irreversible step in the overall desorption process is the desorption of the fully detached oligomer. In other words the desorption rate is determined by the coverage of species with all segments detached from the surface: θ_{IJ} . The rate for such a process would be given by the expression

$$r = \left(\frac{k_B T}{h}\right) \frac{q_{\ddagger}}{q_{IJ}} \exp\left(\frac{-\Delta E}{k_B T}\right) \theta_{IJ} \quad (4)$$

In this expression q_{\ddagger} is the partition function for the transition state to desorption, q_{IJ} is the partition function for the species with all segments detached from the surface, and ΔE is the barrier to desorption of the species with all segments detached from the surface. To make use of such an expression for the rate, it is necessary to rewrite it in terms of the total coverage of adsorbed oligomers, θ , rather than θ_{IJ} over which we have no control. Following from our previous analysis for the desorption of the alkanes,

the rate of desorption can be rewritten as

$$r = \left(\frac{k_B T}{h}\right) \frac{q_{\ddagger}}{q_{IJ}} \frac{1}{\Gamma} \exp\left(\frac{-\Delta A_{IJ}}{k_B T}\right) \exp\left(\frac{-\Delta E}{k_B T}\right) \theta \quad (5)$$

where

$$\Gamma = \sum_{i=0}^I \sum_{j=0}^J \exp\left(\frac{-\Delta A_{ij}}{k_B T}\right) \quad (6)$$

and the ΔA_{ij} are the free energy differences, $\Delta A_{ij} = A_{ij} - A_{00}$, between the species with i C-C bonds and j C-O bonds detached from the surface and the fully attached species with $i = j = 0$.⁸ The rate constant for desorption then becomes

$$\begin{aligned} k_{\text{des}} &= \left(\frac{k_B T}{h}\right) \frac{q_{\ddagger}}{q_{IJ}} \frac{1}{\Gamma} \exp\left(\frac{-\Delta A_{IJ}}{k_B T}\right) \exp\left(\frac{-\Delta E}{k_B T}\right) \\ &= \left(\frac{k_B T}{h}\right) \frac{q_{\ddagger}}{\Gamma} \exp\left(\frac{-(\Delta E_{IJ} + \Delta E)}{k_B T}\right) \end{aligned} \quad (7)$$

It is important to note that the rate constant for oligomer desorption is derived from transition state theory. All the partially detached oligomers are in equilibrium with those that are fully detached, θ_{IJ} , which in turn are in equilibrium with the transition state to desorption. Thus all partially detached species on the surface are in equilibrium with the transition state. It is important not to be misled by Figure 7 into thinking that there is a single pathway to desorption that is restricted to passing through a species with all segments detached, θ_{IJ} . Instead, transition state theory and its expression in eq 7 implicitly invokes an equilibrium between the transition state to desorption and all adsorbed species and this equilibrium is path independent.

Given eq 7 for the desorption rate constant, one then needs a model for the energies, E_{ij} , entropies, S_{ij} , and free energies, A_{ij} , of the partially detached oligomers to evaluate the desorption rate constant at a given temperature. One can then calculate the experimentally determined values of $\Delta E_{\text{des}}^{\ddagger}$ through

$$-\frac{\Delta E_{\text{des}}^{\ddagger}}{k_B} = \frac{d \ln k_{\text{des}}}{d(1/T)} \quad (8)$$

4.2. Energies and Entropies of Adsorbed Polymers.

Our previous study and analysis of the desorption of the alkanes from the surface of graphite yielded an analytical expression for the measured values of $\Delta E_{\text{des}}^{\ddagger}$ as a function of chain length.⁸ In that case the oligomer segments were associated with the C-C bonds and the alkanes were treated as homopolymers. Here we generalize that work to a description of the PEG-DMEs treated as heteropolymers having segments that are the C-C and C-O bonds. To do so, we must develop a model for the energies and the entropies of the PEG-DMEs in their various stages of partial detachment from the graphite surface.

As in the case of the alkanes we will treat the reference state of the PEG-DMEs as the fully adsorbed molecule with its bonds or segments in the all-trans configuration. The coverage of this species is denoted θ_{00} because none of its segments are detached from the surface and its energy is taken to be $E_{00} = 0$. As in the case of the alkanes the energies of species that are partially detached from

the surface are taken to be linear in the numbers of detached segments of each type.

$$\Delta E_{ij} = i\Delta E^{CC} + j\Delta E^{CO} \quad (9)$$

The quantities ΔE^{CC} and ΔE^{CO} are the segment–surface interaction energies and are unknowns in this problem. This is the simplest possible functional form for the energies. One might consider inclusion of interactions between detached segments; however, in our previous study of the desorption of alkanes of lengths similar to those of the PEG-DMEs used in this work we found that inclusion of such interactions yielded only minor contributions to the desorption energies. Interactions between detached segments are likely, however, to have increasing contributions to the desorption energetics for longer chain lengths.

The important contributions to the entropy of the partially detached oligomers come from the many configurations that they can adopt on the surface. The partition function for the partially detached oligomer has two terms for each type of segment and is given by

$$q_{ij} = \frac{\mathcal{I}}{\mathcal{I}(I-j)!} (q_{tg}^{CC})^i \frac{\mathcal{J}}{\mathcal{J}(J-j)!} (q_{tg}^{CO})^j \quad (10)$$

The combinatorial terms account for the number of ways that i of the IC – C bonds can be detached from the surface and j of the JC – O bonds can be detached from the surface. The terms q_{tg}^{CC} and q_{tg}^{CO} are the partition functions describing the trans–gauche conformations about each type of bond. Bonds attached to the surface are restricted to the trans conformation; however, once detached from the surface they are free to adopt trans, +gauche, or –gauche conformations. In the case of the C – C bond the trans–gauche conformational partition function is given by

$$q_{tg}^{CC} = 1 + 2 \exp\left(\frac{-\Delta E_{tg}^{CC}}{k_B T}\right) \quad (11)$$

The first term is for the trans conformation and the second for the two gauche conformations. The quantity ΔE_{tg}^{CC} is the energy difference between the trans and the gauche conformations about a C – C bond. The expression for q_{tg}^{CO} , the partition function for conformations about the C – O bond, has a form similar to that of eq 11.

The differences in energy between the trans and the gauche conformations about detached bonds impart a temperature dependence to the partition functions for the partially detached oligomers. If the trans–gauche energy differences were large, $\Delta E_{tg} \gg k_B T$, then the partition functions would just be $q_{tg} = 1$. Similarly, if they were small, $\Delta E_{tg} \ll k_B T$, the partition functions would be $q_{tg} = 3$ and also independent of temperature. In the case of the PEG-DMEs we can find estimates of the trans–gauche energy differences from ab initio calculations performed by Gejji et al. on $\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$.¹⁷ They found that $\Delta E_{tg}^{CC} = 0.0$ kJ/mol and $\Delta E_{tg}^{CO} = 4.4$ kJ/mol. Although this implies that $q_{tg}^{CC} = 3$, the value of q_{tg}^{CO} is clearly temperature dependent over the temperature range in which the

PEG-DMEs desorb. As we have found with the alkanes, the temperature dependence of the conformational partition functions makes a significant contribution to the measured values of ΔE_{des}^\ddagger .

The entropies of the partially detached oligomers are derived from the partition functions through the Boltzmann equation.

$$S_{ij} = k_B \ln(q_{ij}) \quad (12)$$

The expressions for the energies, E_{ij} , and entropies, S_{ij} , of the partially detached oligomers can be combined with the rate constant defined in eq 7 to determine the value of the ΔE_{des}^\ddagger measured experimentally.

4.3. Analytical Expression for the ΔE_{des}^\ddagger of Hetero-Oligomers. In the case of the alkanes that are considered to be homopolymers it has been possible to derive an analytical expression for the chain length dependence of the ΔE_{des}^\ddagger . This is generalized quite simply to the case of heteropolymers starting with the expression for the desorption rate constant, k_{des} , given in eq 7. First, it is important to realize that Γ , the summation over equilibrium constants (eq 6), is actually a binomial expansion and can be written in closed form.

$$\begin{aligned} \Gamma &= \sum_{i=0}^I \sum_{j=0}^J q_{ij} \exp\left(\frac{-\Delta E_{ij}}{k_B T}\right) \\ &= \left[\sum_{i=0}^I \frac{\mathcal{I}}{\mathcal{I}(I-i)!} (q_{tg}^{CC})^i \exp\left(\frac{-i\Delta E^{CC}}{k_B T}\right) \right] \times \\ &\quad \left[\sum_{j=0}^J \frac{\mathcal{J}}{\mathcal{J}(J-j)!} (q_{tg}^{CO})^j \exp\left(\frac{-j\Delta E^{CO}}{k_B T}\right) \right] \\ &= \left[1 + q_{tg}^{CC} \exp\left(\frac{-\Delta E^{CC}}{k_B T}\right) \right]^I \left[1 + q_{tg}^{CO} \exp\left(\frac{-\Delta E^{CO}}{k_B T}\right) \right]^J \end{aligned} \quad (13)$$

The expression for the energy of the fully detached state, $\Delta E_{I,J}$, is given by eq 9. Finally, the configurational partition function for the transition state to desorption is assumed to be that of the fully detached oligomer, $q_{I,J}$, in which all bonds are free to adopt trans–gauche conformations. With these three terms defined, the expression for the experimentally measured values of the ΔE_{des}^\ddagger is found using eq 8.

$$\Delta E_{des}^\ddagger = I \left[\frac{q_{tg}^{CC} \Delta E^{CC} + (q_{tg}^{CC} - 1) \Delta E_{tg}^{CC}}{q_{tg}^{CC} (1 + q_{tg}^{CC} \exp(-\Delta E^{CC}/k_B T))} \right] + J \left[\frac{q_{tg}^{CO} \Delta E^{CO} + (q_{tg}^{CO} - 1) \Delta E_{tg}^{CO}}{q_{tg}^{CO} (1 + q_{tg}^{CO} \exp(-\Delta E^{CO}/k_B T))} \right] + \Delta E + k_B T \quad (14a)$$

The first two terms of this expression obviously arise from the two types of bonds in the hetero-oligomer. This expression can be simply generalized to oligomers with any number of different types of segments. It is probably also worth pointing out that if one ignores the energy difference between the trans and the gauche conformations about the bonds, then $\Delta E_{tg} = 0$, $q_{tg} = 3$, and q_{tg} is temperature independent. With this approximation the

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expression for the $\Delta E_{\text{des}}^\ddagger$ reduces simply to

$$\Delta E_{\text{des}}^\ddagger = \frac{I\Delta E^{\text{CC}}}{\left(1 + 3 \exp\left(\frac{-\Delta E^{\text{CC}}}{k_{\text{B}}T}\right)\right)} + \frac{J\Delta E^{\text{CO}}}{\left(1 + 3 \exp\left(\frac{-\Delta E^{\text{CO}}}{k_{\text{B}}T}\right)\right)} + \Delta E + k_{\text{B}}T \quad (14b)$$

Although it is not obvious from the form of the expression for $\Delta E_{\text{des}}^\ddagger$ in eq 14 it has a simple physical interpretation. As shown in the previous analysis of alkane desorption, the $\Delta E_{\text{des}}^\ddagger$ is exactly equivalent to

$$\Delta E_{\text{des}}^\ddagger = \langle E^\ddagger \rangle - \langle E \rangle + k_{\text{B}}T \quad (15)$$

where $\langle E^\ddagger \rangle$ is the average energy of the oligomers in the transition state to desorption and $\langle E \rangle$ is the average energy of the partially detached oligomers equilibrated on the surface.⁸ This result is very close to the expression of the Fowler–Guggenheim theorem for the physical significance of the activation barriers measured for reactions in the gas phase.¹⁸

4.4. PEG-DME Desorption Kinetics. The model defined above for the oligomer desorption process results in eq 14 for the $\Delta E_{\text{des}}^\ddagger$, which can be compared with the values of the desorption energies measured for PEG-DMEs of different lengths. The unknowns in this expression are the segment–surface interaction energies ΔE^{CC} and ΔE^{CO} and the barrier to desorption ΔE . The other parameters in eq 14 are the trans–gauche energy differences for the rotational conformations about each bond. These numbers can be determined from other sources such as computational studies of ethers. As mentioned above, values of $\Delta E_{\text{tg}}^{\text{CC}} = 0.0$ kJ/mol and $\Delta E_{\text{tg}}^{\text{CO}} = 4.4$ kJ/mol have been determined for $\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$.¹⁷

Given the seven measured values of the $\Delta E_{\text{des}}^\ddagger$ of the PEG-DMEs, one ought, in principle, to be able to fit the expression for the desorption energy in eq 14 using ΔE^{CC} , ΔE^{CO} , and ΔE as fitting parameters. Unfortunately, because of the stoichiometry of the PEG-DMEs, there is a fixed relationship between the number of C–C and C–O bonds such that $J = 2I + 2$. In other words, the two independent variables in eqs 14a and 14b are not independent for the set of samples that have been studied in this work, and as a result, it is not possible to evaluate ΔE^{CC} and ΔE^{CO} independently. This could only be done with a set of oligomeric ethers in which the numbers of C–C and C–O bonds (I and J in this work) varied independently.

Because the numbers of C–C and C–O bonds in the PEG-DMEs do not vary independently, we have chosen to analyze the measured values of $\Delta E_{\text{des}}^\ddagger$ to obtain an average value of the segment–surface interaction energy, ΔE^{ss} . In other words, we have assumed that the segments are identical and analyzed the data using the expression for a homopolymer. This is simply

$$\Delta E_{\text{des}}^\ddagger = (I + J) \left[\frac{q_{\text{tg}}\Delta E^{\text{ss}} + (q_{\text{tg}} - 1)\Delta E_{\text{tg}}}{q_{\text{tg}} \left(1 + q_{\text{tg}} \exp\left(\frac{-\Delta E^{\text{ss}}}{k_{\text{B}}T}\right)\right)} \right] + \Delta E + k_{\text{B}}T \quad (14c)$$

where $I + J$ is the total number of segments or bonds, ΔE^{ss} is the averaged segment–surface interaction energy,

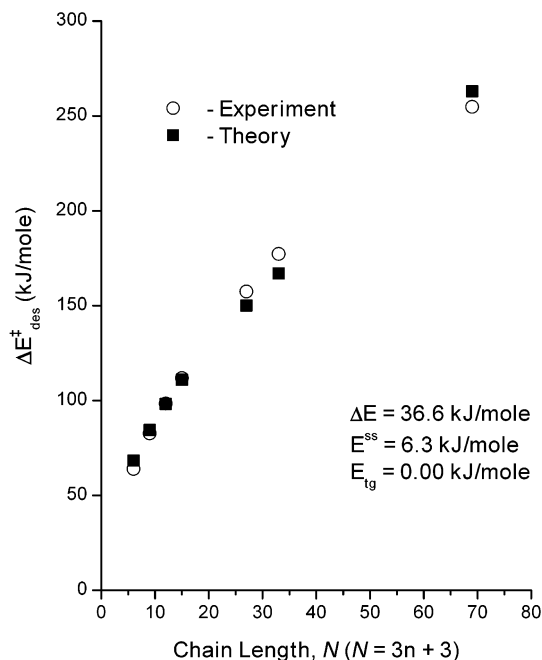


Figure 8. Comparison of the experimentally determined values of $\Delta E_{\text{des}}^\ddagger$ with those predicted by the theory described in this paper by eq 14c. The experimental values of the $\Delta E_{\text{des}}^\ddagger$ are indicated by the open circles (○) and the prediction of the model by the solid squares (■).

and ΔE_{tg} is an average measure of the trans–gauche conformational energy difference. Because there is no a priori way to chose ΔE_{tg} , we have allowed this to be a fitting parameter in the fit of eq 14c to the data obtained for the desorption of the PEG-DMEs from graphite. The results are shown in Figure 8 and reveal that the fit to the data is extremely good. The values found for the segment–surface interaction energy and the trans–gauche energy difference are $\Delta E^{\text{ss}} = 6.3$ kJ/mol and $\Delta E_{\text{tg}} = 0.0$ kJ/mol, respectively. The value for the desorption energy of the fully detached oligomer is $\Delta E = 36.6$ kJ/mol. These parameters are very similar to those that were found for the desorption of the alkanes from the graphite surface.⁸ In the case of the alkanes the segment–surface interaction energy is for the C–C bonds only and has a value of $\Delta E^{\text{CC}} = 6.2$ kJ/mol whereas the value of ΔE is 42 kJ/mol. The principle difference between the fits of the $\Delta E_{\text{des}}^\ddagger$ for the alkanes and the PEG-DMEs is that in the case of the PEG-DMEs we have allowed the value of ΔE_{tg} to vary and found an optimal value of $\Delta E_{\text{tg}} = 0.0$ kJ/mol as a measure of the average trans–gauche energy difference for the PEG-DME bonds. This implies that the value of q_{tg} is 3 and has very little temperature dependence. In other words, the $\Delta E_{\text{des}}^\ddagger$ for the PEG-DMEs are fit very closely by the expression for a homopolymer analogous to eq 14b.

$$\Delta E_{\text{des}}^\ddagger = \frac{(I + J)\Delta E^{\text{ss}}}{\left(1 + 3 \exp\left(\frac{-\Delta E^{\text{ss}}}{k_{\text{B}}T}\right)\right)} + \Delta E + k_{\text{B}}T \quad (14d)$$

As a consequence, the temperature dependence of the q_{tg} does not make any significant contribution to the measured values of $\Delta E_{\text{des}}^\ddagger$ for the PEG-DMEs. This is different from the case of the alkanes for which ΔE_{tg} was held at the

(18) Laidler, K. J. *Chemical Kinetics*, 3rd ed; Harper Collins Publishers: New York, 1987.

known value of $\Delta E_{ig} = 2.5$ kJ/mol and thus resulted in a significant contribution to the measured values of ΔE_{des}^\ddagger .¹⁹

Our model for oligomer desorption does not allow us to predict the absolute magnitudes of the preexponential factors, ν . This is simply because we do not describe the translational, rotational, and vibrational parts of the partition functions for the adsorbed molecules and the molecules in the transition state to desorption. It is the ratio of these partition functions that contributes to the preexponential factors. If we make the assumption that this ratio is independent of the chain length, then we can predict the variation of the measured pre-exponent with chain length. In the case of the alkanes $\log(\nu)$ covers a range of 1.5 for chain lengths in the range $N = 7-44$ whereas we predict that $\log(\nu)$ should vary over a range of 2.5.⁸ The theory predicts, however, that at longer chain lengths the pre-exponents ought to start to decrease significantly. There is no indication of this in our data, and this is something that still needs to be investigated by measuring desorption kinetics at even longer chain lengths.

It is important to discuss the origin of the relatively high value of ΔE , the desorption energy of the fully detached oligomer. Phenomenologically, this arises from the fact that the intercept of the ΔE_{des}^\ddagger versus chain length curve is nonzero. This appears quite obviously in our measurements for the PEG-DMEs shown in Figure 6. It also appeared in our measurements of the ΔE_{des}^\ddagger of the straight chain alkanes on graphite.^{6,7} Furthermore, it appears in all such measurements.^{4,5,20-23} For short alkanes, $H(CH_2)_N H$, having $N \leq 10$ C-C bonds, the measured values of ΔE_{des}^\ddagger can be approximated by $\Delta E_{des}^\ddagger = \Delta E + \Delta E^{CC}N$, where the intercept, ΔE , is substantially greater than the segment-surface interaction energy, ΔE^{CC} . This is an interesting result in its own right and does not appear to be understood. One might imagine that it arises from the fact that the end group interactions

with the surface are greater than those of the internal segments; however, such a model would predict that the segment-surface interaction energies of the C-CH₃ end groups of the alkanes are ~ 5 times higher than those of the internal C-C segments. This seems physically unrealistic. Furthermore, a recent set of measurements comparing the ΔE_{des}^\ddagger for linear and cyclic alkanes on the Cu(100) surface has revealed the same large value of ΔE as is observed for the straight chain alkanes, clearly implying that the phenomenon is not the result of end group effects.²⁴ At this time the origin of the large value of ΔE is not understood.

The fit of eq 14c to the values of the ΔE_{des}^\ddagger as shown in Figure 8 clearly indicates that the model proposed for oligomer desorption from surfaces incorporates the correct physics needed to describe the nonlinear dependence of the ΔE_{des}^\ddagger on chain length. The fact that this same model has been equally successful in the description of the desorption of alkanes from surfaces suggests that the fundamental origin of the nonlinear dependence of the ΔE_{des}^\ddagger on chain length is a general phenomenon that is common to all such straight chain oligomers.

5. Conclusions

The desorption kinetics of poly(ethylene glycol) dimethyl ether oligomers from graphite have been measured and reveal that their ΔE_{des}^\ddagger are nonlinear in chain length. When compared with the results of our previous study of n -alkane desorption from graphite, these findings suggest that the desorption of similar long chain oligomers occur with a common mechanism. The nonlinear dependence of the ΔE_{des}^\ddagger is a result of the fact that entropy favors configurations in the adsorbed oligomers with some segments detached from the surface at temperatures above $T = 0$ K. The values of ΔE_{des}^\ddagger are dictated by the difference in the average energy of the oligomer on the surface, $\langle E \rangle$, and the average energy of the oligomers in the transition state to desorption, $\langle E^\ddagger \rangle$, at the temperature at which the desorption rates are being measured. At the elevated temperatures at which oligomer desorption occurs, the value of $\langle E \rangle$ is much different from the minimum energy state in which all segments are attached to the surface.

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