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# Oligomer desorption during heterogeneous catalytic synthesis of polymers

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## Abstract

Product desorption is the final step in all heterogeneous catalytic processes but is rarely the rate-limiting step. There are, however, exceptions, such as heterogeneous polymerization reactions in which desorption of high molecular weight products can influence the overall reaction rate. In such cases, the apparent activation barrier to desorption, $\Delta E^{\ddagger}_{\mathrm{des}}$, increases with increasing polymer chain length, however, the relationship between the desorption barrier and the desorption energy, $\Delta E_{\mathrm{des}}$, is not straightforward and the scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length is not necessarily linear. Desorption of a series of alkanes, polyethyleneglycol dimethylethers and polyethylene glycols from the surface of graphite has been studied both experimentally and theoretically in order to shed light on the scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with oligomer chain length and on the mechanism of oligomer desorption. In all three cases, the measured values of $\Delta E^{\ddagger}_{\mathrm{des}}$ are non-linear in the chain length. A model has been developed that accurately describes the scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length and shows that the origin of the observed non-linearity is the conformational entropy of the adsorbed oligomers. At elevated temperatures, some fraction of the oligomer segments are detached from the surface and thus do not contribute to the $\Delta E^{\ddagger}_{\mathrm{des}}$ measured at that temperature. One of the consequences of this effect is that the measured value of $\Delta E^{\ddagger}_{\mathrm{des}}$ is dependent on the temperature at which the measurement is made. This effect must introduce a complex temperature dependence into the kinetics and selectivity of heterogeneous catalytic synthesis of long chain polymers.

*Keywords:* Oligomer; Desorption; Catalytic synthesis

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## 1. Introduction

All heterogeneous catalytic reactions involve steps of reactant adsorption, surface reactions and product desorption. Of these three, reactant adsorption and product desorption are rarely the rate-limiting steps. Reactant adsorption is not usually activated and is limited only by diffusion or transport to the catalyst surface. Product desorption is usually considered to be a fairly simple first-order process described by a rate law of the form

$$r_{\mathrm{des}} = k_{\mathrm{des}}\theta, \quad (1)$$

where $\theta$ is the product coverage on the surface and the desorption rate constant, $k_{\mathrm{des}}$, is parameterized in a simple Arrhenius-like form

$$k_{\mathrm{des}} = \nu \exp\left(\frac{-\Delta E^{\ddagger}_{\mathrm{des}}}{k_{\mathrm{B}}T}\right). \quad (2)$$

The quantity $\nu$ is a pre-exponential factor to desorption. The activation barrier to desorption, $\Delta E^{\ddagger}_{\mathrm{des}}$, is often equated with the desorption energy, $\Delta E_{\mathrm{des}}$, because many molecules exhibit no barrier to adsorption. While this description of desorption kinetics is fairly accurate for small, rigid molecules, the work reported in this paper shows that desorption of large flexible molecules, such as polymers or oligomers from surfaces is significantly more complex. This is an important issue, because in the heterogeneous catalytic production of polymers, there must be some molecular weight or product chain length above which desorption becomes the rate-limiting step in the appearance of the product.

Fischer–Tropsch synthesis generates straight chain hydrocarbons with a wide range of lengths from CO

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and $H_2$. The polymers produced in Fischer–Tropsch synthesis grow by insertion of $CH_2$ groups into adsorbed alkyl chains, thereby extending the length of the alkyl chain until it is terminated either by hydrogenation to yield an alkane or by β-hydride elimination to yield an α-olefin [1]. Note that, henceforth we shall refer to the Fischer–Tropsch products as *oligomers* rather than polymers since their molecular weights are lower than those commonly associated with polymers. In the idealized process the insertion and termination probabilities are constants and this leads to the well-known Flory distribution of chain lengths among the products. In reality, however, there are many instances in which the Flory distribution is not observed and the product distribution is enhanced in high molecular weight oligomers, particularly alkanes rather than α-olefins. This is thought to be a result of the fact that α-olefins can re-adsorb onto the catalyst surface, undergo hydrogenation to form alkyl groups and then continue to participate in the insertion and chain growth processes [1–3]. This is a complex process but clearly the residence times of α-olefins on the surface must increase with chain length because the barrier to desorption must increase with chain length. The longer the residence times of the α-olefin on the surface the higher the probability of hydrogenation to form the alkyl chain. This effect must reduce the yield of α-olefins among the high molecular weight products and shift the product distribution from low to high molecular weights. Whether or not this is the dominant influence on the product distribution is not at all clear, however, the residence times of oligomeric α-olefins must influence the Fischer–Tropsch product distribution to some extent.

One of the issues in trying to understand the effects of re-adsorption on the product molecular weight distribution of polymerization processes such as Fischer–Tropsch synthesis is the need to understand the kinetics of oligomer desorption from surfaces. Little attention has been paid to this subject in the field of surface chemistry, which has tended to focus on the adsorption and desorption kinetics of relatively small, rigid species. Desorption kinetics of small molecules are commonly measured using temperature programmed desorption (TPD) methods and often using well-defined single crystal surfaces in vacuum. Desorption of small, rigid molecules from a surface can be considered as translation along a one-dimensional reaction coordinate leading from the adsorbed state to the gas phase. While the atoms in the molecule can vibrate, this type of motion contributes to the partition functions for the adsorbed state and the transition state to desorption and thus to the desorption pre-exponent rather than the desorption barrier. One can easily imagine, however, that desorption of long flexible oligomers from a surface is a much more complex process. As a result of their flexibility, adsorbed polymers are able to adopt a multitude of configurations many of which have lengths, or segments that are partially detached from the surface. These configurations all contribute to the numerous energetically equivalent pathways leading from the fully attached, adsorbed state to the fully detached, desorbed state. In other words, modeling the desorption of a segmented oligomer from a surface must consider the numerous energetically equivalent pathways by which such a molecule can desorb.

As mentioned above, molecular desorption kinetics are commonly described using a first-order desorption model (Eq. (1)) and a desorption rate constant that is parameterized in an Arrhenius-like form (Eq. (2)). Note that in this work the apparent barrier to desorption, $\Delta E^{\ddagger}_{\mathrm{des}}$, is an experimentally determined value that comes from the Arrhenius-like parameterization of the desorption rate constant. A more physically meaningful expression for the desorption rate constant can be derived from transition state theory which gives

$$k_{\mathrm{des}} = \frac{k_{\mathrm{B}}T}{h}\frac{q_{\ddagger}}{q_{\mathrm{ads}}}\exp\left(\frac{-\Delta E^{\ddagger}_{0}}{k_{\mathrm{B}}T}\right). \tag{3}$$

The terms in this expression include the partition function for the adsorbed state, $q_{\mathrm{ads}}$, the partition function for the transition state to desorption, $q_{\ddagger}$, and the difference in the zero-point energies of the adsorbed state and the transition state to desorption, $\Delta E^{\ddagger}_{0}$. It is important to keep in mind that the Arrhenius-like parameterization of the desorption rate constant used to analyze most kinetic data yields a value of the desorption activation barrier that is formally given by

$$\Delta E^{\ddagger}_{\mathrm{des}} = -k_{\mathrm{B}}T\frac{\mathrm{d}\ln(k_{\mathrm{des}})}{\mathrm{d}(1/T)}, \tag{4}$$

and thus is only indirectly related to either the desorption energy, $\Delta E_{\mathrm{des}}$, or the difference in the zero-point energies of the adsorbed state and the transition state to desorption, $\Delta E^{\ddagger}_{0}$. This is one of the key points of this paper and must be considered when trying to model desorption of oligomers from surfaces.

The work described in this paper is based on a set of experiments that have measured the desorption kinetics of oligomeric alkanes ($H(CH_2)_nH$), polyethyleneglycol dimethylethers ($CH_3O(CH_2CH_2O)_nCH_3$) and polyethyleneglycols ($HO(CH_2CH_2O)_nH$) from well-defined graphite surfaces [4–9]. These experiments have shown that the barrier to desorption, $\Delta E^{\ddagger}_{\mathrm{des}}$, measured in a typical temperature programmed desorption experiment is non-linear in the chain length of the desorbing oligomer. The principle contribution of this work is the proposal of a simple model that explains this observation and provides a description of the desorption process that predicts values of $\Delta E^{\ddagger}_{\mathrm{des}}$ that reproduce the observed non-linear scaling with chain length. This model provides insight into phenomena occurring during oligomer desorption that must be relevant to desorption of high molecular weight species produced during Fischer–Tropsch synthesis.

## 2. Experimental

In order to study the desorption kinetics of adsorbed oligomers, temperature programmed desorption (TPD) spectra were obtained using a set of long chain alkanes ($H(CH_2)_nH$, $n = 5–60$), polyethyleneglycol dimethylethers ($CH_3O(CH_2CH_2O)_nCH_3$, $n = 1–22$) and polyethyleneglycols ($HO(CH_2CH_2O)_nH$, $n = 1–22$) adsorbed on the basal plane of graphite. The details of the apparatus, the surface preparation, adsorption of the oligomers and the measurements of the desorption kinetics have been described elsewhere [5]. Briefly, varying coverages of the oligomers were adsorbed on the basal plane of graphite at temperatures of ~120 K. The surface was then heated at constant rates in the range $\beta = 0.1–5$ K/s while using a mass spectrometer to monitor the rate of oligomer desorption into vacuum. All steps were performed under ultra-high vacuum conditions on clean graphite surfaces. The complete set of TPD spectra were analyzed using a number of methods to determine the barriers to desorption, $\Delta E^{\ddagger}_{\text{des}}$, and the pre-exponential factors for desorption, $\nu$ (Eq. (2)) [5,8,9].

## 3. Results

The principle goal of our measurements has been to determine the scaling of the barriers to desorption, $\Delta E^{\ddagger}_{\text{des}}$, with oligomer chain length. In this work, we refer consistently to the experimentally determined desorption barriers as $\Delta E^{\ddagger}_{\text{des}}$. These have been measured by obtaining an extensive set of TPD spectra of three different oligomers with chain lengths ranging from ~5 to ~70 atoms. Fig. 1 illustrates a typical set of TPD curves obtained for $C_{32}H_{66}$ adsorbed on the surface of graphite at initial coverages ranging from significantly less than one monolayer to coverages of several multilayers. These are qualitatively representative of the spectra obtained for the entire set of oligomers on graphite [6,8,9]. At low coverages, there is a single high temperature desorption feature associated with desorption from the monolayer. As the coverage increases, there comes a point at which the second and third layers become populated and desorption from those layers is manifested by a lower temperature desorption feature. We concentrate in this work on desorption from the first layer. The fact that the monolayer desorption peak is independent of temperature suggests that desorption can in fact be treated as a first-order process [10].

The peak desorption temperatures of the oligomers increase monotonically with chain length and are indicative of an increase in $\Delta E^{\ddagger}_{\text{des}}$ with increasing chain length. The TPD peaks for all the alkane monolayers desorbing from graphite are summarized in Fig. 2. Analysis of the TPD spectra to obtain the kinetic parameters for desorption assumes that the rate constant can be parameterized in an Arrhenius-like form (Eq. (2)). One approach has been to use a Redhead analysis of variable heating rate measurements to obtain $\nu$ and $\Delta E^{\ddagger}_{\text{des}}$ independently [10]. A second analysis has integrated the desorption rate equation to predict the TPD curve and then fit the predicted curves to the experimental TPD spectra using $\nu$ and $\Delta E^{\ddagger}_{\text{des}}$ as fitting parameters [5,8,9]. Both methods have yielded a self-consistent set of values for $\nu$ and $\Delta E^{\ddagger}_{\text{des}}$ for the entire set of oligomers desorbing from graphite.

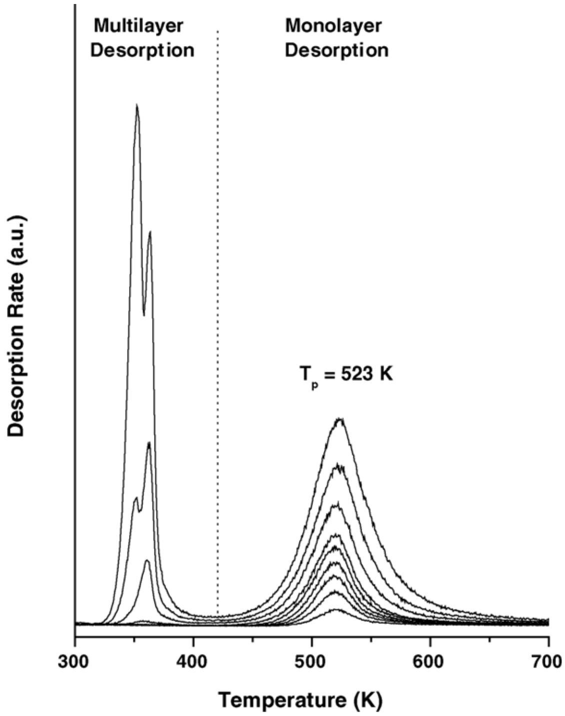

Fig. 1. TPD spectra for $C_{32}H_{66}$ adsorbed on the surface of graphite at 120 K at coverages ranging from submonolayer to multilayer. The desorption peak at 523 K is due to desorption of the monolayer adsorbed directly to the graphite surface. The features at 350 K are assigned to desorption from the multilayers. The monolayer desorption temperature is independent of coverage indicating a first-order desorption process with a coverage independent desorption barrier. The heating rate was 2 K/s and the ion fragment monitored with the mass spectrometer was at $m/q = 57$ ($C_4H_9^+$).

The primary goal of the work has been to determine the scaling of the $\Delta E^{\ddagger}_{\text{des}}$ with oligomer chain length. Fig. 3 shows the $\Delta E^{\ddagger}_{\text{des}}$ for all three oligomers as a function of chain length and clearly shows that the $\Delta E^{\ddagger}_{\text{des}}$ scales non-linearly with chain length for all three. The curves plotted through the data for the $n$-alkanes and the PEG–DMEs are simple empirical fits of curves having the functional form $\Delta E^{\ddagger}_{\text{des}} = \alpha + \beta n^{\gamma}$ and clearly represent the data quite accurately. The values of $\Delta E^{\ddagger}_{\text{des}}$ for the PEGs deviate from those for the PEG–DMEs at low molecular weight. It is important to note two features of this data. The first is that the measurements of the pre-exponents to desorption reveal that they are roughly independent of chain length and have values on the order of $\nu \approx 10^{19}\ \text{s}^{-1}$. The second and more important feature of this data is that $\Delta E^{\ddagger}_{\text{des}}$ is measured from desorption peaks occurring at temperatures ranging from ~160 K for the shortest oligomers to >700 K for the longest. Our analysis of polymer desorption kinetics must take this fact into account in order to

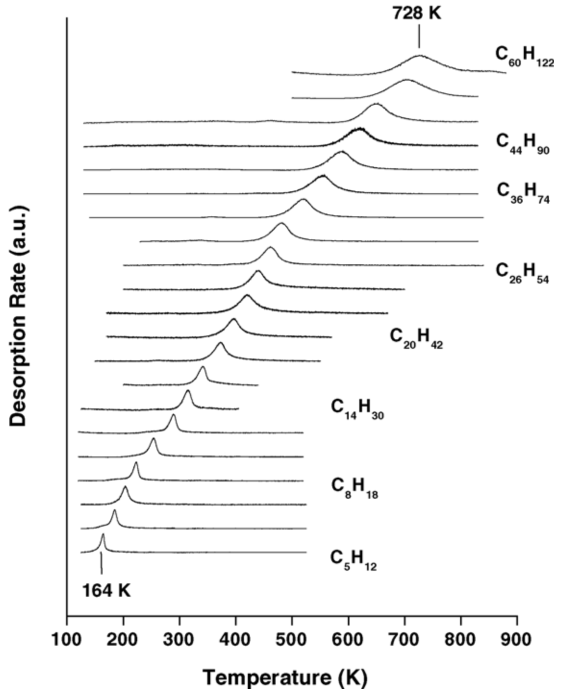

Fig. 2. TPD spectra of all *n*-alkanes studied following adsorption of approximately one monolayer on the graphite surface at 120 K. Both the desorption peak temperature and peak width increase with increasing chain length. The peak desorption temperatures of each *n*-alkane have been used to estimate their barriers to desorption, $\Delta E^{\ddagger}_{\mathrm{des}}$. All spectra were generated using a mass spectrometer to monitor the signals at either $m/q = 57$ ($C_4H_9^+$) or $m/q = 71$ ($C_5H_{11}^+$) during heating. The heating rate was 2 K/s in all cases.

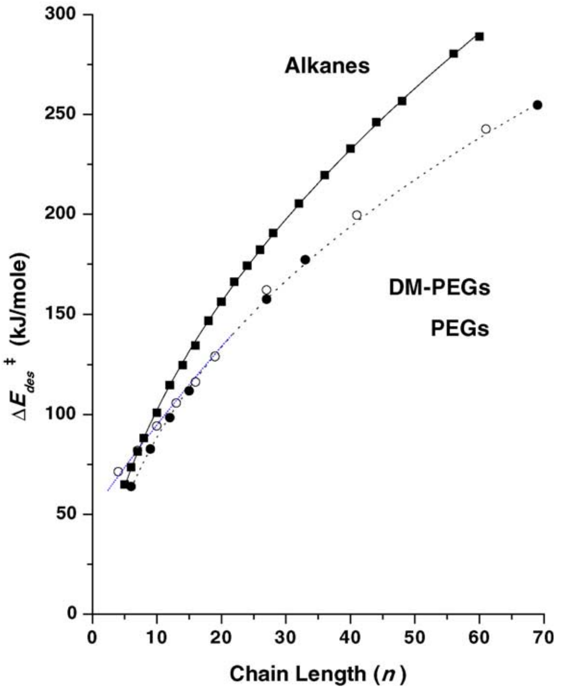

Fig. 3. Experimentally determined desorption barriers of alkanes (■), polyethyleneglycol dimethylethers (●, DM–PEGs) and polyethyleneglycols (○, PEGs) adsorbed on graphite. All three sets of data reveal non-linear scaling of the $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length. The solid curve is a fit of the empirical form $\Delta E^{\ddagger}_{\mathrm{des}} = \alpha + \beta n^{\gamma}$ to the experimentally determined values of $\Delta E^{\ddagger}_{\mathrm{des}}$ for the *n*-alkanes. The dashed curve is a fit of the same functional form to $\Delta E^{\ddagger}_{\mathrm{des}}$ for the DM–PEGs. Both fits reproduce the non-linear scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length very well. At short chain lengths where end group effects can appear, the desorption barriers for the PEGs deviate from those of the DM–PEGs.

correctly predict the non-linear scaling of the $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length.

## 4. Discussion

In discussing the origins of the non-linear scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with oligomer chain length it is important to reiterate the fact that the rate constant measured experimentally is simply parameterized (Eq. (2)) in a form that yields $\Delta E^{\ddagger}_{\mathrm{des}}$ from the experimental data. The physical significance of $\Delta E^{\ddagger}_{\mathrm{des}}$ is not obvious because it is related to the transition state rate constant, $k_{\mathrm{des}}$, through Eq. (4). For small, rigid molecules the partition functions for the adsorbed state, $q_{\mathrm{ads}}$, and the transition state, $q_{\ddagger}$, describe translational, rotational, and vibrational degrees of freedom. The partitions functions for these degrees of freedom can have a significant impact on the magnitude of the pre-exponential factor, however, they have fairly weak temperature dependences and thus they do not contribute significantly to the measured value of $\Delta E^{\ddagger}_{\mathrm{des}}$. Therefore, for small rigid molecules the value of $\Delta E^{\ddagger}_{\mathrm{des}}$ will differ from $\Delta E^{\ddagger}_{0}$ by some small multiple of $k_{\mathrm{B}}T$ and thus $\Delta E^{\ddagger}_{\mathrm{des}}$ is a close approximation to $\Delta E^{\ddagger}_{0}$ and is also a good estimate of the desorption energy, $\Delta E_{\mathrm{des}}$.

Desorption of oligomeric species from surfaces is complicated by the fact that they are flexible and can adopt numerous configurations on the surface at elevated temperatures. As a consequence, the partition functions that are used to describe the oligomer in the adsorbed state and in the transition state to desorption must include description of all possible configurations. This can have a profound effect on the value of $\Delta E^{\ddagger}_{\mathrm{des}}$ that is measured experimentally. If one thinks about the polymer as a chain of *I* independent segments that are free to attach and detach from the surface (Fig. 4), then the conformational states of the molecules can be enumerated in terms of the number of detached segments, *i*. The partition function for the adsorbed polymer becomes

$$q_{\mathrm{ads}} = \sum_{i=0}^{I} g_i \exp\left(\frac{-\Delta E_i}{k_{\mathrm{B}}T}\right), \tag{5}$$

where $\Delta E_i$ is the difference in zero-point energy between the conformation with *i* segments detached from the surface, $E_i$, and the zero-point energy of the fully attached state, $E_0$. The term $g_i$ is the degeneracy of those conformations with *i* segments detached from the surface. The transition state has all *I* segments detached from the surface and thus a partition function simply given by

$$q_{\ddagger} = g_I. \tag{6}$$

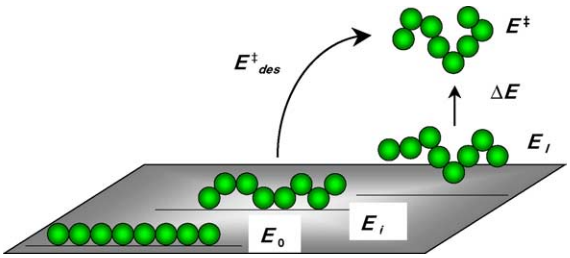

Fig. 4. Hypothetical configurations adopted by an *n*-alkane chain of length $I = 8$ on the graphite surface. The ground state is one in which the *n*-alkane molecule lies in an all-*trans* conformation and has no detached segments ($i = 0$). An intermediate state is depicted in which the *n*-alkane chain is adsorbed in a configuration with four of its eight segments detached ($i = 4$). The adsorbed state that exists prior to desorption is also depicted and is one with all $I$ segments detached. The segments attach and detach from the surface reversibly and thus the configurations are in equilibrium with one another.

In the common formulation of transition state theory, the zero-point energy of the transition state with respect to that of the fully adsorbed state, $\Delta E_0^{\ddagger}$, is included in the Boltzmann factor of Eq. (3). In order to evaluate the transition state theory rate constant for desorption, $k_{\text{des}}$, one needs a model for the energies, $E_i$, and the degeneracies, $g_i$, of the partially detached oligomers in the adsorbed phase and in the transition state for desorption.

The model used to describe the segmental nature of the adsorbed chains equates the segments with the C–C and C–O bonds in the adsorbed alkanes and polyethylene glycols [7,8]. In other words, an alkane with $n$ carbon atoms has $I = n - 1$ segments. We consider the ground state of the system to be the oligomer adsorbed with all segments (bonds) attached to the surface and in the all-*trans* conformation. This is consistent with numerous low temperature scanning tunneling micrographs of alkanes adsorbed on the graphite surface [11–16]. In partially detached configurations those bonds, which are detached from the surface, are free to adopt both *trans* and *gauche* conformations. The simplest model for the energies of the partially detached configurations is

$$\Delta E_i = i \cdot \Delta E^{\text{CC}}, \tag{7}$$

where $\Delta E^{\text{CC}}$ is a segment–surface interaction parameter. The degeneracies of the partially detached states are given by

$$g_i = \frac{I!}{i!(I-i)!}(q_{\text{tg}})^i. \tag{8}$$

The combinatorial term simply accounts for the number of ways of detaching $i$ of $I$ segments from the surface. The quantity $q_{\text{tg}}$ is a partition function that accounts for the fact that once they are detached from the surface, bonds can adopt both *trans* and *gauche* conformations. In the simplest model the *trans*–*gauche* partition function would take a value of $q_{\text{tg}} = 3$. If one includes the fact that there is an energy difference, $\Delta E_{\text{tg}} = 2.5$ kJ/mol [17], between the *trans* and the *gauche* conformations, this becomes

$$q_{\text{tg}} = 1 + 2\exp\left(\frac{-\Delta E_{\text{tg}}}{k_{\text{B}}T}\right). \tag{9}$$

Eqs. (7)–(9) serve as the basis for describing the energies and entropies (through the partition functions) of all partially detached states of adsorbed oligomers at elevated temperatures. These can then be combined to give the transition state theory expression for the desorption rate constant, $k_{\text{des}}$.

The temperature dependence of the desorption rate constant formulated on the basis of the model described above ultimately predicts the value of the desorption barrier that one measures experimentally (Eq. (4)). In the simplest formulation with $q_{\text{tg}} = 3$ one finds that

$$\Delta E^{\ddagger}_{\text{des}} = I\left(\frac{\Delta E^{\text{CC}}}{1 + 3\exp\left(\frac{\Delta E^{\text{CC}}}{k_{\text{B}}T}\right)}\right) + \Delta E + k_{\text{B}}T. \tag{10a}$$

If one includes the temperature dependent of the *trans*–*gauche* partition function, $q_{\text{tg}}$, as given in Eq. (9), then

$$\Delta E^{\ddagger}_{\text{des}} = I\left[\frac{q_{\text{tg}}\Delta E^{\text{CC}} + (q_{\text{tg}} - 1)\Delta E_{\text{tg}}}{q_{\text{tg}}\left(1 + q_{\text{tg}}\exp\left(\frac{-\Delta E^{\text{CC}}}{k_{\text{B}}T}\right)\right)}\right] + \Delta E + k_{\text{B}}T. \tag{10b}$$

These expressions contain two empirical parameters, $\Delta E^{\text{CC}}$ and $\Delta E$ that must be determined by fitting Eq. (10) to the experimental values of $\Delta E^{\ddagger}_{\text{des}}$ [7]. As mentioned, $\Delta E^{\text{CC}}$ is associated with the segment–surface interaction energy. The origin of the quantity $\Delta E$ is somewhat more empirical and will be discussed below. Fig. 5 shows the fits of Eq. (10b) to the experimentally determined values of $\Delta E^{\ddagger}_{\text{des}}$. The symbols in Fig. 5 are the predictions of Eq. (10b) obtained by using the known temperatures of oligomer desorption and the curves are the empirical fits to the experimentally determined values of $\Delta E^{\ddagger}_{\text{des}}$. As shown previously in Fig. 3, these curves are extremely good representations of the experimentally determined values of $\Delta E^{\ddagger}_{\text{des}}$. Quite clearly, the predictions of our model provide a very good representation of the non-linear scaling of $\Delta E^{\ddagger}_{\text{des}}$ with chain length. The fits predict values of $\Delta E^{\text{CC}} = 6.2$ kJ/mol for the *n*-alkanes and $\Delta E^{\text{CC}} = 6.3$ kJ/mol for the PEG–DMEs. In the case of the PEG–DMEs, this number represents an average segment–surface energy for the C–C and the C–O bonds interacting with the graphite surface. The value of $\Delta E^{\text{CC}} = 6.2$ kJ/mol for the *n*-alkanes is consistent with measurements using small alkanes adsorbed on a number of surfaces [18].

Note that the expressions for $\Delta E^{\ddagger}_{\text{des}}$ in Eq. (10) are both linear in the number of segments, $I$, in the oligomer. What then is the origin of the apparent non-linearity in the scaling of $\Delta E^{\ddagger}_{\text{des}}$ with chain length? As mentioned earlier, it is important to keep in mind the fact that the oligomer desorption kinetics are measured over a wide temperature range with the peak desorption temperature varying from ~160 K for the short molecules to >700 K for the longest

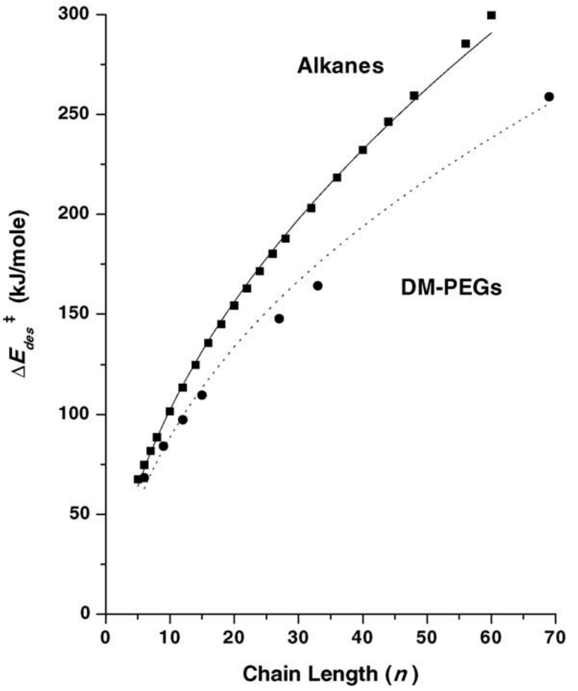

Fig. 5. Values of $\Delta E^{\ddagger}_{\mathrm{des}}$ predicted by Eq. (10b) for the alkanes (■) and by a similar expression for the polyethyleneglycol dimethylethers (●) as a function of chain length. The curves are the empirical fits to the experimentally determined values of $\Delta E^{\ddagger}_{\mathrm{des}}$. The predictions of the model for oligomer desorption reproduce the non-linear scaling of the experimentally determined $\Delta E^{\ddagger}_{\mathrm{des}}$ very well.

oligomers used in this work. The expressions for $\Delta E^{\ddagger}_{\mathrm{des}}$ are temperature dependent and, as a consequence, the barrier that one measures to the desorption of an oligomer will depend on the temperature at which the measurement is made. At 0 K, the measured values of the desorption barriers would simply be

$$\Delta E^{\ddagger}_{\mathrm{des}}(0) = I \cdot \Delta E^{\mathrm{CC}} + \Delta E. \tag{11}$$

As is easily discernable from Eq. (10a), the measured barrier will decrease with increasing measurement temperature. Hence, as the chain length and the desorption temperature increase, the deviation of the measured value of $\Delta E^{\ddagger}_{\mathrm{des}}$ from Eq. (11) will increase leading to the apparent non-linear scaling with length.

The quantity $\Delta E$ is an empirical constant that appears in Eq. (10). It arises from the fact that the desorption barriers for the alkanes on graphite and on all other surfaces studied experimentally, have a non-zero intercept, $\Delta E$, as the chain length goes to zero [18]. The origin of this is not understood at this point and several possibilities have been discussed recently but without resolving the problem. Recent work suggests that more careful measurements of the pre-exponential factors for the desorption of the alkanes will show that they increase with chain length in the short chain regime and that proper accounting for the pre-exponents will result in values of $\Delta E^{\ddagger}_{\mathrm{des}}$ that intercept the origin as the chain length drops to zero [19,20]. Our preliminary analysis of this contribution to polymer desorption indicates that this will not significantly change the non-linearity of the scaling of $\Delta E^{\ddagger}_{\mathrm{des}}$ with chain length but it would eliminate the need to include $\Delta E$ in the expressions for $\Delta E^{\ddagger}_{\mathrm{des}}$ (Eq. (10)). Further analysis of the pre-exponents for desorption is needed to resolve these issues for the longer chain alkanes.

The measured value of $\Delta E^{\ddagger}_{\mathrm{des}}$ as expressed in Eq. (10) does have a physical significance although it is clearly not just the difference in the zero-point energies of the adsorbed oligomer and the transition state to desorption, $\Delta E^{\ddagger}_{0}$. One can show that the expressions in Eq. (10) are identically equal to

$$\Delta E^{\ddagger}_{\mathrm{des}} = \langle E^{\ddagger} \rangle - \langle E_{\mathrm{ads}} \rangle + \frac{1}{2} k_{\mathrm{B}} T, \tag{12}$$

or in other words, the difference in the average energies of the adsorbed oligomer, $\langle E_{\mathrm{ads}} \rangle$, and the transition state to desorption, $\langle E^{\ddagger} \rangle$ [7]. In the adsorbed state, the oligomer has some fraction of its segments detached from the surface and that fraction increases with increasing temperature, increasing $\langle E_{\mathrm{ads}} \rangle$. This manifests itself in a decrease in $\Delta E^{\ddagger}_{\mathrm{des}}$ with increasing temperature. Given the energies and entropies of the partially detached alkanes, as predicted by our model, one can calculate the fraction of detached segments at any given temperature, Fig. 6. One of the interesting features of the model is that it predicts that the fraction of detached segments at any temperature is independent of chain length. Not surprisingly, at low temperatures all segments are attached to the surface, however, at high temperatures, significant

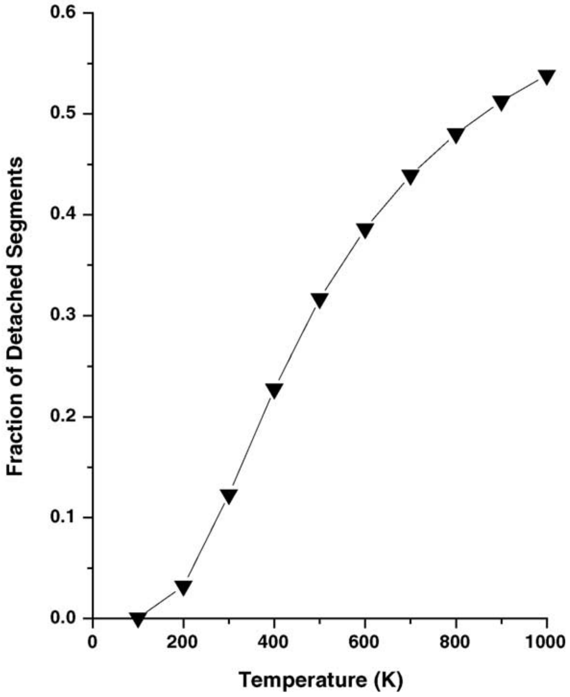

Fig. 6. The fraction of detached segments in an $n$-alkane adsorbed on graphite as a function of temperature. This fraction is independent of the chain length. The fraction of detached segments increases with increasing temperature, thus reducing the barrier to desorption for those long alkanes that desorb at high temperatures.

fractions of the segments can be detached from the surface. For example, at 700 K at which the longest chain alkanes used in our study desorb, our model predicts that on average ~40% of the segments are detached from the surface. The desorption energy that one measures at that temperature is then determined by the average fraction of segments remaining attached to the surface.

Although the experiments performed in this work have been limited to saturated alkanes and polyethylene glycols, the basic results should be quite general in nature. The kinetics of oligomer desorption from surfaces are quite complex. The measured barrier to desorption clearly increases with chain length, but not in a trivial fashion. Although it does scale linearly with chain length at a given temperature, the barriers to desorption are temperature dependent. The fact is that the kinetics of oligomer desorption do have an impact on the selectivity of heterogeneous polymerization catalysis, be it of alkanes and olefins in the Fischer–Tropsch process or in any other polymerization reaction. In the case of Fischer–Tropsch catalysis, readsorption of olefins onto the catalyst surface can result in hydrogenation and further chain growth. The fact that the barrier to desorption increases with chain length increases the residence time of olefins adsorbed or readsorbed on the surface and thereby increases the probability of hydrogenation and further chain growth. This reduces the selectivity towards olefin production in the high molecular weight fraction of the Fischer–Tropsch synthesis products.

Independent of its relevance to polymerization catalysis the problem of oligomer desorption from surfaces is interesting in its own right. The work presented here sheds some light on the process but the problem is far from completely understood. There are a number of interesting issues that arise from this work. What is the origin of the non-zero intercept, $\Delta E$, of the desorption barrier with chain length [18]? Some works suggests that it may simply arise from poor measurement of the pre-exponents to desorption and that these should vary with chain length [19,20]. Certainly, further work is needed to understand the chain length dependence of the pre-exponents to desorption. Another issue is the influence of end groups on the desorption kinetics. Comparison of our measurements of the $\Delta E^{\ddagger}_{\text{des}}$ of polyethyleneglycols and polyethyleneglycol dimethylethers shows that end group effects are observable but that they only appear at short chain lengths (Fig. 3). Finally, our model does not include and does not need to include interactions between the detached segments of the oligomers, at least in the chain length regime investigated. At some chain length, however, the desorption kinetics of long oligomeric species from surfaces must be influenced by the interactions between segments that are detached from the surface. Finally, the work presented here poses the experimental challenge of observing or detecting the partially detached segments of adsorbed oligomers at elevated temperatures. The continued study of simple, well-defined systems, such as the ones used in this work will shed light on the physics of oligomer desorption and on processes that are relevant in more complex systems, such as those of catalytic polymerization reactions.

## 5. Conclusions

The flexibility of polymers and oligomers on surfaces allows them to exist in a large number of configurations at elevated temperatures and thus in a wide distribution of partially detached states having a range of energies. This has an observable impact on the desorption kinetics of oligomers from surfaces. The desorption barriers, $\Delta E^{\ddagger}_{\text{des}}$, are temperature dependent and their scaling with chain length is complex. A simple statistical model is sufficient to capture this temperature and length dependent scaling of oligomer desorption barriers. These effects contribute, at least in part, to the non-Flory distributions of products from catalytic polymerization processes, such as Fischer–Tropsch synthesis.

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