Multi-Scale Simulation of the Thermal Desorption of Large Molecules from Solid Surfaces

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ABSTRACT

We use molecular-dynamics simulations and importance sampling to obtain transition-state theory rate constants for thermal desorption of an \( n \)-alkane series from Pt(111). These simulations indicate that the binding of a large molecule to a solid surface is a complex phenomenon involving many local minima. The existence of local minima invalidates the interpretation of thermal desorption as a single, first-order rate process. Because the number of local minima increases with increasing chain length, \( n \)-alkane adsorption becomes increasingly dominated by entropy for longer chains. Consequently, the binding energy increases in a less-than-linear way with increasing chain length. Our results provide a quantitative explanation for results and trends in recent experimental studies.

Keywords: Molecular Dynamics, Transition-State Theory, Thermal Desorption

1 INTRODUCTION

\( n \)-Alkanes have been studied by numerous groups as a model for large molecular adsorbates [1]–[4]. On a variety of different solid surfaces, the \( n \)-alkane binding energies are experimentally observed to increase with increasing chain length [1]–[4]. This trend has been loosely associated with a binding conformation in which an \( n \)-alkane molecule binds “flat” with its long axis parallel to the surface, in the all-\( \text{trans} \) conformation. To support this idea, low-temperature, ultra-high vacuum studies with various techniques [1], [2], [4] provide evidence that this “flat” and all-\( \text{trans} \) conformation is dominant. Given that the alkane-surface interaction is likely to be dominated by van der Waals dispersion forces, which are pairwise, it is expected that the binding energies of “flat” and all-\( \text{trans} \) alkanes should increase linearly with increasing chain length. In contrast to this expectation, \( n \)-alkane binding energies have been experimentally observed to increase in a less-than-linear way with increasing chain length. For example, Paserba and Gellman showed that the binding energies for a series of 21 \( n \)-alcanes on graphite, with 5 ≤ \( N \) ≤ 60 carbons, increases as \( N^{3/2} \) [3].

To understand the origins of these observations, we consider the thermal desorption of a series of \( n \)-alkanes, ranging from ethane (\( C_2H_6 \)) to \( n \)-decane (\( C_{10}H_{22} \)) from Pt(111). Thermal desorption of molecules in this series on Pt(111) has been studied experimentally with temperature-programmed desorption (TPD) [1], [2] and Bishop et al. pointed out that the segmental (per carbon) binding energy for this series decreases with increasing chain length [1]. We focus on the low-coverage limit of a single molecule on the Pt(111) surface. We show that \( n \)-alkanes bind to the surface in various local minima, which include gauche conformers, in addition to the global-minimum, all-\( \text{trans} \) binding state. Because the number of local minima increases with increasing chain length, \( n \)-alkane adsorption becomes increasingly dominated by entropy for longer chains. Consequently, the binding energy increases in a less-than-linear way with increasing chain length. Our results provide a quantitative explanation for the experimental trends.

2 MODEL AND METHODS

Our model system is described elsewhere [5]. Briefly, we model \( n \)-alkanes using the united-atom (UA) model. Because of its high frequency, the C-C stretch is constrained to its equilibrium value in the fluid phase using the SHAKE algorithm. Intermolecular potentials that are well-established in the literature are used for the remaining degrees of freedom. We describe the alkane-surface interaction using the UA model, in which the pair-wise UA-Pt interaction is modeled by a Lennard-Jones (12-6) potential, with parameters adjusted to match recent, experimental estimates of the low-coverage binding energy of \( n \)-butane to Pt(111) [2]. Finally, we model the Pt(111) surface as a five-layer slab with 64 atoms per layer. We model the motion of atoms in the top three layers, so that the surface acts as a heat bath and aids in achieving a canonical distribution of alkane configurations.

We characterize \( n \)-alkane desorption using transition-state theory (TST), in which the desorption rate con-
stant is given by [6]

$$k_{TST} = \frac{1}{2} \left( \frac{2k_BT}{\pi m} \right)^\frac{1}{2} \int \frac{\delta (R - R_0)e^{-V(R)/k_BT}}{R} dR \int \frac{e^{-V(R)/k_BT}}{R} dR,$$

(1)

where the integrals cover the entire configurational space when the adsorbate is near the surface, including the TST dividing surface between the adsorbed and desorbed state. In Eq. 1, $R^0$ is the set of coordinates characterizing the TST dividing surface, $V(R)$ is the potential energy at $R$, $k_B$ is the Boltzmann constant, $T$ is temperature, and $m$ is the mass of the adsorbate. We define a single TST dividing surface to be a plane parallel to the surface and at the incipient height $h$, unique for each alkane, such that the alkane-surface interaction is zero beyond $h$. With this definition, a molecule is a free, gas-phase molecule at the transition state.

Although it is, in principle, straightforward to evaluate $k_{TST}$ using MD, thermal desorption occurs over time scales much greater than can be probed in MD simulations. Thus, we cannot adequately sample the TST dividing surface. To improve sampling of the transition-state region, we evaluate the average of Eq. (1) using importance sampling [7]. Representing the TST dividing surface as a thin “box” with width $b$, the canonical average of Eq. (1) can be written as [6]

$$k_{TST} = \frac{1}{2} \left( \frac{2k_BT}{\pi m} \right)^\frac{1}{2} \frac{1}{b} \frac{\langle \delta (F(R)) \rangle_W}{\langle \frac{1}{W} \rangle_W}. \quad (2)$$

Here, $W(R)$ is a function designed to improve sampling of the transition-state region. Importance sampling has been used to quantify rare-event processes, such as surface diffusion [6] and thermal desorption [8]. A unique feature here is the form that we use for the function $W$, which is given by

$$W(R) = \exp \left( \frac{s-1}{s} \frac{V(R)}{k_BT} \right), \quad (3)$$

with $s \geq 1$. For $s = 1$, the denominator in Eq. (2) is unity and the average in the numerator becomes the canonical average of Eq. (1). For $s > 1$, Eq. (2) has a simple interpretation: We run a MD simulation at a high temperature $sT$, for which thermal desorption occurs over a convenient time scale for MD simulations. By computing the value of $W$ at each time step, we can evaluate the averages in Eq. (2) and obtain $k_{TST}$ for the desired temperature $T$.

3 Results and Discussion

We found that the TST rate constants obey Arhenius behavior. Effective TST activation energies $E_{d,TST}$ and preexponential factors $\nu_{0,TST}$ are obtained by fitting TST rate constants to the form

$$k_{TST} = \nu_{0,TST} \exp(-E_{d,TST}/k_BT). \quad (4)$$

These are shown in the first two columns of Table 1, where we see that $E_{d,TST}$ and $\nu_{0,TST}$ both increase with increasing chain length. It should be noted that for the larger molecules, the preexponential factors take on values significantly greater than the “typical” value of $10^{13}$ s$^{-1}$. This can, in part, be attributed to the gain in entropy at the transition state when a molecule desorbs. For large molecules, there is a significant gain in conformational degrees of freedom (and, hence, entropy) upon desorption. We also show experimental (TPD) estimates of the binding energy in Table 1 as $E_{d,\text{expt}}$. While we see that both the TST and the experimental binding energies increase less-than-linearly with increasing chain length, the experimental values for hexane-decane fall below TST estimates. In comparing our results to experiment, it is important to consider that in the experimental TPD studies for hexane-decane [1], desorption energies are obtained by using the Redhead equation for first-order desorption with the assumption that $\nu_0 = 10^{13}$. Thus, to achieve desorption parameters consistent with experiment, we simulate TPD experiments [10]. The resulting TPD activation energies are shown in Table 1, where it can be seen that the agreement with experiment is excellent. Thus, we see that the experimental binding energies for $C_6-C_{10}$ are suppressed in Redhead analysis of TPD spectra.

Although the chain-length dependence of the experimental binding energies can be partially attributed to the approximate Redhead analysis of the TPD data, our apparent TST binding energies still exhibit a less-than-linear increase with increasing chain length. To resolve the origins of this trend, we obtain the binding energies of $n$-alkanes in various conformational states by minimizing their total energies at 0 K [10]. $n$-Butane has only one torsion angle for rotation about its central C-C bond. There are two conformers associated with this torsion angle, trans and gauche. $n$-Hexane has three bonds around which torsion could occur. In the fluid phase, this would allow for six different torsions and 16 different conformers. However, the number of local minima is greater for adsorbed hexane because a given conformer can exhibit multiple minima in binding to the surface. For example, in the all-trans conformation, $n$-hexane has a global and a local minimum. A schematic of these minima can be viewed in reference [11]. Moving up to $n$-octane and decane, the number of different gauche conformers and local minima increases. For example, in a previous study [11], we showed that octane and decane have two and three local minima, respectively, in just the all-trans conformation. To assess the role of local minima in thermal desorption and to
Table 1: Experimentally determined barriers (kJ/mol) and preexponential factors (s\(^{-1}\)).

<table>
<thead>
<tr>
<th>Length</th>
<th>(\nu_{0,TST})</th>
<th>(E_{d,TST})</th>
<th>(E_{d,TPD})</th>
<th>(E_{d,expt})</th>
<th>(E_{d,trans})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(8.41 \times 10^{11})</td>
<td>29.69</td>
<td>31.88</td>
<td>32.0 [9]</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>(1.00 \times 10^{13})</td>
<td>52.03</td>
<td>50.05</td>
<td>50.6 [2]</td>
<td>55.8</td>
</tr>
<tr>
<td>6</td>
<td>(6.11 \times 10^{13})</td>
<td>69.09</td>
<td>65.22</td>
<td>61.75 [1]</td>
<td>84.18</td>
</tr>
<tr>
<td>8</td>
<td>(3.99 \times 10^{13})</td>
<td>82.84</td>
<td>72.24</td>
<td>71.91 [1]</td>
<td>112.36</td>
</tr>
<tr>
<td>10</td>
<td>(4.94 \times 10^{15})</td>
<td>91.05</td>
<td>77.50</td>
<td>77.27 [1]</td>
<td>139.95</td>
</tr>
</tbody>
</table>

Properly account for entropic effects, we use MD simulations to quantify the fraction of time that each molecule spends in its various conformational states [10]. These studies show that the molecules spend less time in the all-trans state as the chain length increases.

With many conformational states available for alkane binding, each with a unique binding energy to the surface, it is natural to inquire which binding energy or what quantity is reflected in experimental binding energies. Our studies indicate that this quantity is not the all-trans, global-minimum binding energy. To show this, we include the all-trans binding energies from our calculations in Table 1. We see that the all-trans binding energies are higher than the TST values and that there is a divergence between the two values as the chain length increases.

REFERENCES