

Thermal Desorption of Large Molecules from Solid Surfaces

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(Received 5 June 2002; published 21 October 2002)

We use molecular-dynamics simulations and importance sampling to obtain transition-state-theory rate constants for thermal desorption of an n -alkane series from Au(111). We find that the binding of a large molecule to a solid surface involves different types of local minima. The preexponential factors increase with increasing chain length and can be substantially larger than typical estimates for small molecules. Our results match recent experimental studies and indicate that a proper treatment of conformational isomerism and entropy, heretofore not found in coarse-grained models, is essential to quantitatively describe the thermal desorption of large molecules from solid surfaces.

DOI: 10.1103/PhysRevLett.89.196103

PACS numbers: 68.43.De, 68.43.Fg, 68.43.Mn, 68.43.Vx

The equilibrium and dynamics of large molecules at surfaces are important in assembly, catalysis, thin films, lubrication, molecular electronics, and microfluidics. With the current emphasis toward miniaturization of technology, tighter control is needed of molecular processes at surfaces. Increased understanding of the equilibrium structures and dynamics of large molecular adsorbates is important toward this end.

n -Alkanes, with chemical formula C_NH_{2N+2} , are prototypical large molecules that exhibit many of the rich features associated with molecular adsorption. These nonpolar, chainlike molecules are relatively inert and they physically adsorb to a variety of solid surfaces, including metals [1–7], metal oxides [8], and graphite [9–11]. n -Alkane desorption energies are experimentally observed to increase with increasing chain length, a trend that has been loosely associated with n -alkanes aligning their C-C bonds parallel to the surface, in the all-*trans* conformation. To support this idea, ultrahigh vacuum studies with various techniques [2–4,7,10,11] provide evidence that the “flat” and all-*trans* conformation occurs almost exclusively at low temperatures. Since the alkane-surface interaction is most likely dominated by van der Waals dispersion forces, which are pairwise, it is expected that the desorption energy should increase linearly with increasing chain length. In contrast, n -alkane binding energies have been experimentally observed to increase in a less-than-linear way with increasing chain length [1,2,9]. In perhaps the best example of this trend, Paserba and Gellman used temperature-programmed desorption (TPD) to measure the desorption energies for a series of 21 n -alkanes, with $5 \leq N \leq 60$ carbons, adsorbed to graphite [9]. They showed that the desorption energy for this series increases as $N^{1/2}$, and they attributed this trend to the existence of partially bound alkane conformers near the desorption temperature. In this Letter, we consider the microscopic basis for such a model.

The desorption dynamics of large molecules can be characterized by both an activation energy E_d and a

prefactor ν_0 , so that the rate constant k is given by $k = \nu_0 \exp(-E_d/k_B T)$. The activation energy is emphasized in most studies and ν_0 is assumed to take on the “typical” value of 10^{13} s^{-1} . In this Letter, we show that the preexponential factor for large molecules can be substantially larger than the typical value.

We use molecular dynamics (MD) to simulate the thermal desorption of a series of n -alkanes, ranging from methane (CH_4) to n -dodecane ($C_{12}H_{24}$) from Au(111), focusing on the low-coverage limit of a single alkane molecule. To describe these molecules, we adopt the united-atom (UA) model [12], in which CH_N ($N = 2-4$) groups are modeled as single interaction centers. We describe the UA-Au interaction using a Lennard-Jones (12-6) potential, truncated at a distance of $\sim 8.2 \text{ \AA}$, with parameters adjusted to match the desorption energy of n -hexane from Au(111) [1]. We assume that each UA interacts equally with the surface, neglecting possible variations in the polarizability for C and H atoms in different local environments. From studies of n -alkanes in the fluid phase, we expect these variations to be small [13]. Finally, we model the Au(111) surface as a five-layer slab with 64 atoms per layer. Atoms in the bottom two layers are fixed to their bulk, equilibrium positions. Atoms in the middle layer are maintained at a constant temperature to provide a heat bath for atoms in the top two layers. We represent Au-Au interactions using a Lennard-Jones (12-6) potential with parameters chosen to yield the lattice constant and the bulk cohesive energy of Au. It should be noted that the main role of the surface is to mimic the fcc(111) structure of Au(111) and to provide a heat bath for the adsorbate.

We obtain n -alkane desorption rates using transition-state theory (TST), in which the desorption rate is given as a canonical average of the flux of adsorbed molecules passing through the transition state to the vacuum above. This average can be written as [14]

$$k_{\text{TST}} = \frac{1}{2} \left(\frac{2k_B T}{\pi m} \right)^{1/2} \frac{\int_{\mathbf{R}} \delta[F(\mathbf{R})] e^{-V(\mathbf{R})/k_B T} d\mathbf{R}}{\int_{\mathbf{R}} e^{-V(\mathbf{R})/k_B T} d\mathbf{R}}, \quad (1)$$

where the integrals cover the entire configurational space when the adsorbate is near the surface, including the TST dividing surface. $F(\mathbf{R})$ is defined such that $F(\mathbf{R}) = 0$ at the TST dividing surface, $V(\mathbf{R})$ is the potential energy at \mathbf{R} , and m is the mass of the adsorbate. Because molecular alkane adsorption is not activated experimentally [1] or in our model, there are no saddle points on the potential-energy surface to designate as transition states for desorption. We define the TST dividing surface to be a plane parallel to the substrate and at the incipient center-of-mass height h , such that the alkane-surface interaction is always zero at h . Thus, a molecule assumes its fluid-phase distribution of configurations at the transition-state surface. If the sticking probability is unity up to the desorption temperature, then the TST description is exact [15].

Since thermal desorption occurs over time scales much greater than can be probed in MD simulations, we cannot evaluate Eq. (1) with conventional MD. Thus, we use importance sampling [16]. Representing the TST dividing surface as a thin “box” with width b , the canonical average of Eq. (1) can be written as [17]

$$k_{\text{TST}} = \frac{1}{2} \left(\frac{2k_B T}{\pi m} \right)^{1/2} \frac{1}{b} \frac{\langle \frac{\delta[F(\mathbf{R})]}{W} \rangle_W}{\langle \frac{1}{W} \rangle_W}. \quad (2)$$

Here, $W(\mathbf{R})$ is a weighting function designed to improve sampling of the transition-state region. Importance sampling has been used previously to quantify rare-event processes, such as thermal desorption [15] and surface diffusion [17]. A unique feature here is the form that we use for the function W , which is given by

$$W(\mathbf{R}) = \exp \left[\left(\frac{s-1}{s} \right) \frac{V(\mathbf{R})}{k_B T} \right], \quad (3)$$

with $s \geq 1$. 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 the MD time scale. By computing the value of W at each time step, we evaluate the averages in Eq. (2) and obtain k_{TST} for the desired temperature T .

We obtained TST rate constants in the range between 50 and 400 K. The value of k_{TST} at each temperature is an average over typically 2000 trajectories. Arrhenius plots of $\ln(k_{\text{TST}})$ vs $1/T$ were linear, and we determined effective TST activation energies $E_{d,\text{TST}}$ and prefactors $\nu_{0,\text{TST}}$ using the relation $k_{\text{TST}} = \nu_{0,\text{TST}} \exp(-E_{d,\text{TST}}/k_B T)$. These are shown in Table I, where we see that $E_{d,\text{TST}}$ and $\nu_{0,\text{TST}}$ both increase with increasing chain length.

Small prefactors, around 10^{11} – 10^{12} are expected for simple adsorbates (such as methane) on smooth metal surfaces [15]. Similarly, Weaver *et al.* [3] obtained a prefactor of 7×10^{13} —a value close to ours—in a recent experimental study of *n*-butane desorption from Pt(111). The prefactors for the larger molecules are significantly greater than the typical value of 10^{13} s^{-1} . These values reflect a growing difference between the adsorbed and the

gas-phase (transition-state) entropies, which are rendered exactly in MD simulations. Motions that are free in the gas phase (e.g., translation and rigid-body rotation) are hindered on the surface. To date, we are aware of only two experimental studies of long-chain molecule desorption in which large prefactors have been reported [9,18]. In recent TPD studies of *n*-alkane desorption [9] from graphite, Paserba and Gellman found prefactors around 10^{19} s^{-1} for several alkanes containing between 7 and 44 carbon atoms. Although the difference that we find between ν_0 for octane and dodecane is comparable to theirs, their values are 3 to 4 orders of magnitude larger than ours. This discrepancy may be partially attributed to the different surfaces, as well as the fact that their experiments were carried out at a finite coverage.

In most relevant experimental studies of alkane desorption, prefactors around 10^{13} s^{-1} have been assumed. We consider the ramifications of this assumption by simulating TPD for our alkane series. To simulate TPD, we solve the first-order rate equation for the *n*-alkane fractional coverage as a function of time t , using the TST rate parameters in Table I to characterize the rate. When the temperature is increased linearly with time $T = T_0 + \beta t$, where β is the heating rate, the desorption rate goes through a maximum at a peak temperature of T_p . The Redhead equation for first-order desorption is used in many experimental studies to relate T_p to rate parameters $\nu_{0,\text{TPD}}$ and $E_{d,\text{TPD}}$ through the expression

$$\frac{E_{d,\text{TPD}}}{k_B T_p} = \ln \left(\frac{\nu_{0,\text{TPD}} T_p}{\beta} \right) - 3.64. \quad (4)$$

Simulated TPD spectra for a typical experimental heating rate of $\beta = 2 \text{ K/s}$ are shown in Fig. 1.

Using Eq. (4), we extract TPD binding energies $E_{d,\text{TPD}}$ from the TPD spectra by assuming that $\nu_{0,\text{TPD}} = 10^{13} \text{ s}^{-1}$. By simulating TPD with the correct (TST) rate parameters and (incorrectly) analyzing the results assuming that $\nu_{0,\text{TPD}} = 10^{13}$, we mimic the corresponding experimental study [1]. The resulting TPD activation energies are shown along with the TST values in Fig. 2, where we also include the experimental desorption energies $E_{d,\text{expt}}$ for alkanes on Au(111) [1]. The experimental

TABLE I. TST prefactors $\nu_{0,\text{TST}}$ (s^{-1}) and barriers $E_{d,\text{TST}}$ (kJ/mol).

Alkane	$\nu_{0,\text{TST}}$	$E_{d,\text{TST}}$
CH ₄	$(1.5 \pm 0.2) \times 10^{12}$	11.1 ± 0.2
C ₂ H ₆	$(1.3 \pm 0.1) \times 10^{13}$	21.7 ± 0.4
C ₄ H ₁₀	$(4.3 \pm 0.6) \times 10^{13}$	40 ± 1
C ₆ H ₁₄	$(3.7 \pm 0.6) \times 10^{14}$	62 ± 2
C ₈ H ₁₈	$(2.5 \pm 0.4) \times 10^{15}$	82 ± 2
C ₁₀ H ₂₂	$(1.0 \pm 0.6) \times 10^{16}$	98 ± 4
C ₁₂ H ₂₆	$(2.8 \pm 0.6) \times 10^{16}$	121 ± 5

and simulated TPD activation energies agree within 3 kJ/mol. In the experimental study [1], Wetterer *et al.* attributed the nonlinear increase of the alkane binding energy to differences in the polarizability of C-C and C-H bonds in different chain environments (e.g., central vs terminal bonds), which lead, for example, to a stronger molecule-surface interaction for a CH₃ group than for a CH₂ group. Our results suggest a different interpretation of the experiments [1]: Because of their incorrect assumption of $\nu_0 = 10^{13}$, they underestimated the desorption energies of the larger molecules to an increasing extent with increasing chain length, creating an exaggerated and artificial nonlinear trend. Here, we find that this leads to incorrect estimates of the activation energy: In Fig. 2, we see that the TPD desorption energies are less than the “true” TST values by up to 24 kJ/mol for dodecane. Our studies also indicate that analyses of surface kinetics must be extremely thorough to ascertain the correct rate parameters. In Fig. 1, we include TPD spectra that we simulated using the TPD desorption parameters. Despite vast differences between the TST and TPD rate parameters, their simulated TPD spectra are similar. If rate parameters can be corroborated by methods other than TPD, then a sufficiently wide temperature range should be probed to determine them uniquely.

In an effort to understand the trends in the alkane activation energies and prefactors, we consider the model developed by Paserba and Gellman [9]. In their model, different segments of a molecule can detach from the surface, resulting in a series of partially attached conformers with binding energies given by nE_s , where n is the number of attached segments and E_s is the segment binding energy. With a microscopic perspective, we realize that partially attached conformers cannot occur to the extent predicted in their model, as bond length and bond angle constraints prohibit it: It is not possible to

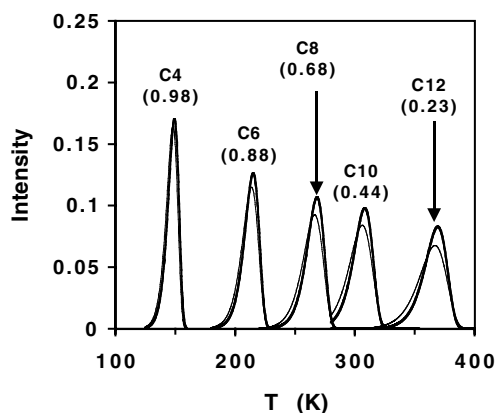


FIG. 1. Simulated TPD spectra for butane (C4) through dodecane (C12) using the TST rate parameters in Table I (heavy lines) and TPD rate parameters (thin lines). The percent of the time that a molecule is in the *trans* state at its peak temperature is also indicated.

have “on”-“off” nearest-neighbor (or even third-neighbor) bonds at distances approaching the cutoff of the molecule-surface interaction (8 Å). We performed a search for various binding states of the *n*-alkanes by minimizing their total energies. These studies reveal a significant number of adsorbed conformers. However, they are not the on-off conformers assumed by Paserba and Gellman [9].

First, we observe *trans-gauche* conformers, which originate from rotation around C-C bonds. These conformers exist in the fluid phase [19], where the energy differences between them are relatively small. The smallest molecule to exhibit these conformers is *n*-butane, which has one torsion angle for rotation about its central C-C bond. *n*-Butane exhibits a *trans* and a *gauche* conformer, which bind to Au(111) with energies of 46.5 and 40.1 kJ/mol, respectively. The binding energy of the global-minimum *trans* conformer is 4 times as large as the segmental binding energy (here, the binding energy of methane) of $E_s = 11.6$ kJ/mol. Since the difference between the binding energies of the *trans* and *gauche* conformers is less than E_s , the on-off model [9] does not accurately describe them. In the fluid phase, the *trans* conformer of *n*-butane is favored over the *gauche* by about 3 kJ/mol, which is less than the energy difference on the surface. When a molecule binds to a solid surface, its total energy is governed by both the intramolecular potential and the molecule-surface interaction. The energy difference between the *trans* and the *gauche* conformers reflects both of these contributions.

In considering the various binding configurations of *n*-hexane, we identify a second type of surface conformer, also not taken into account in the on-off model [9]. Each of the *trans-gauche* conformers can have several local minima in binding to the surface. For example, in the all-*trans* conformation, *n*-hexane has a global and a local minimum that bind with energies of 69.9 and

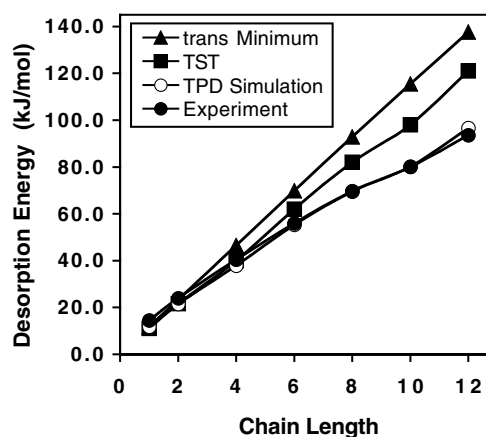


FIG. 2. Desorption activation energies vs chain length obtained from the global minimum, all-*trans* configuration, TST, simulated TPD, and experiment [1].

66.7 kJ/mol, respectively. A schematic of similar minima for Pt(111) can be viewed elsewhere [20], where we see that the local minimum is achieved mainly by rigid-body rotation of the molecule parallel to the surface plane. When the torsion angle associated with the second (or fourth) C-C bond in hexane is in the *gauche* state, there are two local minima, with binding energies of 62.3 and 61.7 kJ/mol. These minima are distinguished primarily by their tilt angle perpendicular to the surface plane. Moving up to the larger molecules, the number of local minima increases. For example, octane and decane have two and three local minima, respectively, in just the all-*trans* conformation. As the size of a molecule increases, the discreteness of the substrate lattice becomes less significant and there are more ways to match UAs to optimal binding locations on the surface. Thus, we expect the number of local minima to increase with increasing chain length.

We now consider the impact of surface conformers on alkane desorption energies. A key idea is that the number of surface conformers increases with increasing chain length. Energy differences between local and global minima become a smaller fraction of the binding energy for larger molecules, increasing the extent to which local minima are populated with increasing chain length. As a result, molecules are less likely to be in the global-minimum, all-*trans* conformation at desorption temperatures. This can be seen in Fig. 1, where we include the fraction of the time that each molecule is in the all-*trans* configuration at T_p . Thus, thermal desorption occurs as a series of parallel rate processes from various minima, whose increasing number leads to a less-than-linear increase in the desorption energy with increasing chain length. As we see in Fig. 2, the all-*trans* binding energies are higher than the TST values and there is a divergence between the two values as the chain length increases. We note that the global-minimum, all-*trans* binding energy is directly proportional to the segmental binding energy, while the TST desorption energy for large molecules is not.

Finally, the increase in local minima with chain length could also impact the prefactors for larger molecules. As the chain length increases, chain conformations will approach a continuum of states. It seems possible in this limit that the entropy of an adsorbed chain could attain its fluid-phase scaling with chain length. This would lead to constant prefactors for sufficiently large molecules, as observed experimentally for large alkanes on graphite [9].

In summary, we show that the binding of a large molecule to a solid surface can involve many local minima, which originate from *trans-gauche* conformers and local minima in the molecule-substrate potential. As the chain

length increases, the number of these minima increases and they become increasingly accessible at desorption temperatures, promoting a less-than-linear increase in the desorption energy. We show that the desorption prefactors can be significantly greater than the typical value of 10^{13} . While we focus on *n*-alkanes desorbing from Au(111), the phenomena that we observe here are general and should be generally present in the adsorption and desorption of large molecules from solid surfaces.

Support for this work is from the Petroleum Research Fund administered by the ACS.

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