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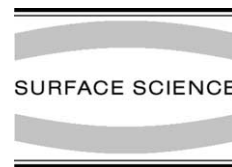
Ryan Z. Lei
Carnegie Mellon University

Andrew J. Gellman
Carnegie Mellon University

B E. Koel
University of Southern California

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Desorption energies of linear and cyclic alkanes on surfaces: anomalous scaling with length

Ryan Z. Lei^a, Andrew J. Gellman^{a,*}, B.E. Koel^b

^a Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, USA

^b Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

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Abstract

The desorption energies, $\Delta E_{\text{des}}^{\ddagger}$, of linear and cyclic alkanes on the Cu(111) and Pt(111) surfaces have been measured and compared to the values of the $\Delta E_{\text{des}}^{\ddagger}$ measured on a number of other surfaces. For sets of short linear and cyclic alkanes ($n\text{-C}_N\text{H}_{2N+2}$ and $c\text{-C}_N\text{H}_{2N}$, $N = 3\text{--}12$) desorbing from single crystalline surfaces the $\Delta E_{\text{des}}^{\ddagger}$ scale linearly in chain length with the form $\Delta E_{\text{des}}^{\ddagger}(N) = \Delta E + \Delta E^{\text{CH}} \cdot N$. The quantity ΔE^{CH} can be equated with a segmental contribution to the $\Delta E_{\text{des}}^{\ddagger}$, however, the physical origin of the non-zero intercept, ΔE , is not clear. Comparison of the intercepts, for the linear and cyclic alkanes show that they are similar to one another on the Cu(111) surface and on the Pt(111) surface. This comparison rules out the possibility that ΔE arises from endgroup effects. Scaling of the $\Delta E_{\text{des}}^{\ddagger}$ against the polarizabilities, α , of the alkanes also reveals that ΔE cannot arise from the scaling of the polarizability with chain length. We discuss other possible origins of ΔE including lattice commensurability effects, temperature, and desorption order.

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Keywords: Alkanes; Surface energy; Molecular dynamics; Thermal desorption

1. Introduction

A number of studies have measured the desorption kinetics of linear alkanes from a variety of single crystal metal surfaces and examined the scaling of the desorption energies, $\Delta E_{\text{des}}^{\ddagger}$, with chain length [1–8]. For short linear alkanes ($\text{C}_N\text{H}_{2N+2}$, $N = 3\text{--}12$) one finds that the $\Delta E_{\text{des}}^{\ddagger}$ can be approximated well by a linear expression of the

form $\Delta E_{\text{des}}^{\ddagger}(N) = \Delta E + \Delta E^{\text{CH}} \cdot N$, where ΔE^{CH} is the incremental increase in $\Delta E_{\text{des}}^{\ddagger}$ per methylene segment. At the simplest level one expects that $\Delta E_{\text{des}}^{\ddagger}$ should be simply proportional to the chain length. Unexpectedly, however, the linear scaling of the $\Delta E_{\text{des}}^{\ddagger}$ with chain length, N , reveals a non-zero intercept, ΔE , which can be several times greater than the segmental increment, ΔE^{CH} . The magnitude of ΔE is quite surprising and its origin is not obvious. In fact, a recent molecular dynamics study of the desorption of alkanes from the Au(111) surface showed that a united atom model of the alkane–surface interaction predicts values of $\Delta E_{\text{des}}^{\ddagger}$ that are proportional to chain

* Corresponding author. Tel.: +1-4122683848; fax: +1-4122687139.

E-mail address: ag4b@andrew.cmu.edu (A.J. Gellman).

length with the value of ΔE being much less than ΔE^{CH} [9]. Although the existence of non-zero intercepts, ΔE , in experimental data has been noted in the past, its origin is an interesting problem that has not yet been resolved [3,10]. This paper attempts to address the physical origin of ΔE .

A non-zero intercept, ΔE , in plots of the alkane desorption energy, $\Delta E_{\text{des}}^{\ddagger}$, versus chain length has been observed by a number of researchers. Alkanes with chain lengths of $N = 3$ –12 have been adsorbed and desorbed from single crystal surfaces of several metals and graphite. The results of these measurements will be discussed in more detail later in this paper. With one exception, all of the measurements were made by using temperature programmed desorption (TPD) to measure $\Delta E_{\text{des}}^{\ddagger}$. The exception is a set of isothermal measurements of the desorption kinetics of hexane through dodecane on the Au(111) surface made using isothermal helium atom reflectivity [1]. These were accompanied by TPD measurements of these and lower molecular weight alkanes from the Au(111) surface. For all of the surfaces studied the segmental increment in $\Delta E_{\text{des}}^{\ddagger}$ with chain length lies in the range $\Delta E^{\text{CH}} = 5$ –7.5 kJ/mol. What is most interesting from the perspective of this paper is that the intercept, ΔE , of $\Delta E_{\text{des}}^{\ddagger}$ can assume values that are two to six times as high as the segmental increment in $\Delta E_{\text{des}}^{\ddagger}$.

If a sufficiently large range of chain lengths is considered, there is no reason to expect that $\Delta E_{\text{des}}^{\ddagger}$ should be linear in the chain length. At temperatures above 0 K, entropy effects in very long chains will cause some fraction of the C–C bonds in the adsorbed alkanes to adopt gauche configurations and some fraction of the segments to be detached from the surface. Indeed measurements of the desorption kinetics of n -alkanes with a very wide range of chain lengths ($\text{C}_N\text{H}_{2N+2}$, $5 \leq N \leq 60$) from the surface of a single crystal of graphite revealed these effects [7,11,12]. The intent of that work was to test the limits to which $\Delta E_{\text{des}}^{\ddagger}$ can be described as linear in the chain length and ultimately to determine the origins of this non-linearity. It was possible to describe $\Delta E_{\text{des}}^{\ddagger}$ as linear in chain length for a narrow range of chain lengths, e.g. $N = 5$ –10. Over the entire range of chain lengths, however,

$\Delta E_{\text{des}}^{\ddagger}$ has a non-linear dependence on chain length. A mechanism for the desorption process and a model for the energy and entropy of n -alkanes on the graphite surface were proposed that quantitatively reproduced the non-linearity in $\Delta E_{\text{des}}^{\ddagger}$. That model predicts a value of $\Delta E^{\text{CH}} = 6.2$ kJ/mol for the increment per segment. From the perspective of the work described in this paper, however, it is important to note that even in that model for the desorption of long chain alkanes, the intercept of $\Delta E_{\text{des}}^{\ddagger}$ is non-zero and has a value of $\Delta E = 41$ kJ/mol. In other words, even values of $\Delta E_{\text{des}}^{\ddagger}$ measured over a very wide range of chain lengths reveal a significant value of ΔE .

Several physical phenomena might give rise to a non-zero value of ΔE . The most obvious would be end effects arising from the fact that one does not expect the methyl endgroups of alkanes to give the same contribution to $\Delta E_{\text{des}}^{\ddagger}$ as the internal methylene segments. That possibility is explicitly tested in this work by comparing the values of $\Delta E_{\text{des}}^{\ddagger}$ for linear and cyclic alkanes with the same chain lengths. Endgroup effects arise if methyl groups have different binding affinities to surfaces than methylene groups. The goal of our experimental investigation is to determine the differences in binding affinities of methyl and methylene groups by measuring $\Delta E_{\text{des}}^{\ddagger}$ of n -alkanes and their cyclic counterparts on Cu(111) and Pt(111) surfaces. Cyclic alkanes have no methyl endgroups so the difference between $\Delta E_{\text{des}}^{\ddagger}$ of linear and cyclic alkanes of the same length might be attributed to the difference in the binding affinities of the methylene and methyl groups. As will be shown, the difference between the binding strengths of the methylene and methyl groups is negligible and cannot account for the fact that ΔE is several times the value of ΔE^{CH} .

In addition to endgroup effects, there are other possible origins of the non-zero value of ΔE . Bishop et al. have suggested that ΔE arises as a result of an artifact in the way in which the TPD spectra are analyzed to determine $\Delta E_{\text{des}}^{\ddagger}$ [3]. They have suggested that the presence of islands or other organized structures on the surface can lead to variations in the effective reaction order for desorption. As a result, simply using a first-order equation for all chain lengths will lead to mis-

leading results when considering chains of different lengths. It is also important to recognize that both the alkanes and the crystalline substrate have periodic structures and that commensurability effects might give rise to non-linear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on N , even for a narrow range of short chain lengths. Finally, the binding of the alkanes to these surfaces occurs through weak van der Waals interactions and thus examination of the relationship between $\Delta E_{\text{des}}^{\ddagger}$ and the polarizabilities, α , of the alkanes might shed light on the origins of ΔE . All of these possibilities will be considered in our discussion of this problem.

2. Experimental

All experiments on the Cu(111) surface were performed in an ultra-high vacuum (UHV) chamber with a base pressure of $<10^{-10}$ Torr achieved through use of a cryo-pump and titanium sublimation pump. The chamber is equipped with two leak valves fitted with stainless steel dosing tubes. The chamber is also equipped with an Ametek Dycor quadrupole mass spectrometer (QMS), which has a mass range of 1–200 amu and is capable of monitoring up to eight masses simultaneously during TPD experiments.

A copper single crystal cut to within 0.5° of the (111) plane was used for experiments presented in this paper. The crystal was mounted by spotwelding it between two Ta wires at the end of a manipulator. Once mounted on the manipulator, the Cu(111) sample could be cooled to ~ 90 K through contact with a liquid nitrogen reservoir and heated resistively at a constant rate. The crystal temperature was measured using a chromel–alumel thermocouple spotwelded to the rear face of the crystal. The front surface of the crystal was cleaned by Ar^+ ion sputtering with cycles of heating from 90 to 1000 K and then holding it at 1000 K for 100 s. The condition of the surface following this initial treatment was highly reproducible as determined by alkane adsorption and desorption. Cycles of Ar^+ sputtering and annealing to 1000 K were conducted after adsorption and desorption of each pair of linear and cyclic alkanes of a given chain length to ensure a clean surface.

Within the UHV chamber the Cu(111) sample was positioned adjacent to the stainless steel dosing tube and approximately 2 cm from an aperture to the QMS. The TPD experiments consisted of three steps: adsorption, desorption, and detection. The adsorption step entailed cooling the sample to ~ 90 K and exposing its surface to alkane vapor at pressures ranging from 10^{-9} to 10^{-8} Torr for periods of 30–200 s. Desorption of the adsorbed molecules was induced by heating the sample at a constant rate from 100 to 700 K. Desorbing species including any decomposition products were monitored during heating by the QMS. In all cases, adsorption and desorption of the linear and cyclic alkanes was molecular and reversible with no indication of decomposition.

The measurements on the Pt(111) surface were performed in a similar manner in a second UHV chamber equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) optics, and a UTI 100C QMS for TPD measurements. The sample could be cooled to 95 K and heated resistively to 1200 K. It was cleaned using a previously published procedure [13]. TPD experiments were performed by adsorbing the alkanes at low temperature and then heating at 4 K/s.

The set of short chain *n*-alkanes [*n*- C_3H_8 , 98+%; *n*- C_5H_{12} , 99+%; *n*- C_6H_{14} , 99+%; *n*- C_7H_{16} , 99+%; *n*- C_8H_{18} , 99+%; *n*- $\text{C}_{10}\text{H}_{22}$, 99+%] and cyclic alkanes [*c*- C_3H_6 , 99+%; *c*- C_5H_{10} , 99+%; *c*- C_6H_{12} , 99+%; *c*- C_7H_{14} , 98+%; *c*- C_8H_{16} , 99+%; *c*- $\text{C}_{10}\text{H}_{20}$, 98+%] used in this investigation was purchased from Strem Chemicals. All compounds were purified before use by using a series of freeze–pump–thaw cycles intended to remove high vapor pressure contaminants.

3. Results

3.1. TPD spectra of linear and cyclic alkanes

TPD spectra were obtained for a set of short chain linear and cyclic alkanes (C_3 , C_5 – C_8 , and C_{10}) in order to measure their $\Delta E_{\text{des}}^{\ddagger}$ from the Cu(111) surface. Fig. 1 shows TPD spectra of *n*- C_6H_{14} desorbing from the Cu(111) surface following

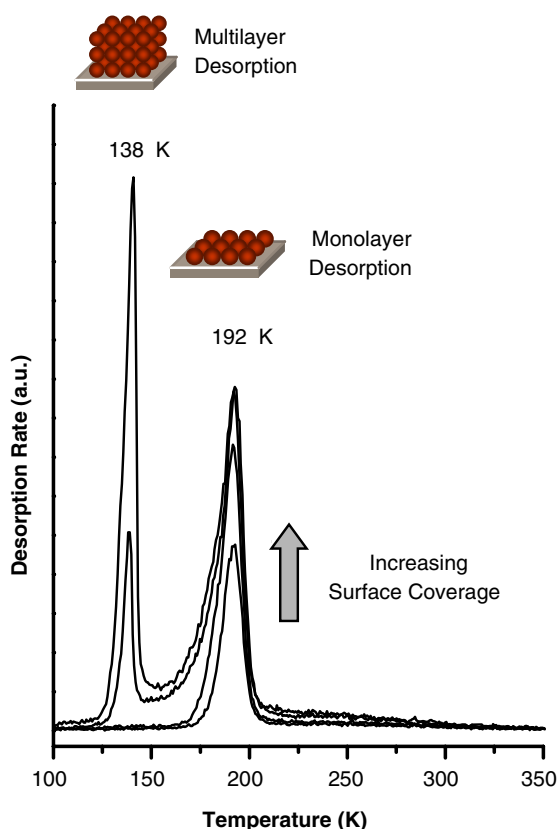


Fig. 1. TPD spectra of C_6H_{14} desorbing from the Cu(111) surface obtained as a function of increasing coverage following adsorption at 90 K. Spectra were generated by monitoring the signal at $m/q = 41$ ($C_3H_5^+$) during heating. The heating rate was $\beta = 2$ K/s.

adsorption of various different coverages at 90 K. The spectra were generated by monitoring the QMS signal at a mass-to-charge ratio of $m/q = 41$ ($C_3H_5^+$) during heating at 2 K/s. Two additional values of $m/q = 57$ ($C_4H_9^+$) and $m/q = 43$ ($C_3H_7^+$) were also monitored in order to detect desorption of decomposition products. No decomposition of $n-C_6H_{14}$ or any of the other linear or cyclic alkanes was observed during desorption from the Cu(111) surface. At low coverages, the spectrum shows a desorption feature at 192 K, indicative of monolayer desorption. The monolayer peak increased in intensity as the coverage increased and saturated in intensity. At that point a second feature indicative of multilayer desorption appeared at 138 K. Fig. 1 shows distinct, well-resolved monolayer and multi-

layer desorption peaks characteristic of desorption from a homogeneous surface. The monolayer and multilayer peak desorption temperatures are consistent with those found for $n-C_6H_{14}$ desorbing from the Cu(100) surface using a 3 K/s heating rate (196 and 135 K) [8], and a 5 K/s heating rate (202 and 145 K) [2].

The TPD spectra obtained using other linear and cyclic alkanes on the Cu(111) and Pt(111) surfaces were similar to those of Fig. 1. The monolayer peak desorption temperatures are listed in Table 1. Peak desorption temperatures for n -alkanes on Pt(111) were obtained from Bishop et al. [3]. Monolayer peak desorption temperatures from the Cu(111) surface are consistent with those found by Teplyakov et al. [8] for $n-C_5H_{12}$ (172 K), $c-C_5H_{10}$ (166 K), $n-C_6H_{14}$ (196 K), and $c-C_6H_{12}$ (181 K) desorbed from Cu(100) using a heating rate of 3 K/s. As a result of the interest in vibrational mode softening in alkanes on metal surfaces there have been a number of studies of $c-C_6H_{12}$ adsorption and desorption on the Cu(111) surface [14–17]. The reported desorption temperatures are 165 K in one study and 178 K at a heating rate of 3 K/s in the other. In summary, the TPD spectra indicate simple reversible molecular adsorption and desorption of the alkanes on all surfaces. The observation that the monolayer peak desorption temperatures were independent of coverage indicates that desorption is a first-order kinetic process.

3.2. Pre-exponential factor and ΔE_{des}^\ddagger for alkane desorption from Cu(111)

In order to compare the desorption kinetics of linear and cyclic alkanes we have determined both the desorption energy, ΔE_{des}^\ddagger , and the pre-exponential factor, v , of the rate constant for desorption from the Cu(111) surface. Analysis of TPD measurements made with varying heat rates, β , allows independent calculation of ΔE_{des}^\ddagger and v [18] through the relation

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{v}{RT_p}\right) - \frac{\Delta E_{des}^\ddagger}{RT_p}. \quad (1)$$

A plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for measurements made at different heating rates should be linear

Table 1
Values of T_p and $\Delta E_{\text{des}}^\ddagger$ for linear and cyclic alkanes on Cu(111) and Pt(111)

Hydrocarbon	Cu(111)		Pt(111)	
	T_p (K)	$\Delta E_{\text{des}}^\ddagger$ (kJ/mol) ^a	T_p (K)	$\Delta E_{\text{des}}^\ddagger$ (kJ/mol) ^b
Propane, <i>n</i> -C ₃ H ₈	119	40.2		
Cyclopropane, <i>c</i> -C ₃ H ₆	117	41.7		
Pentane, <i>n</i> -C ₅ H ₁₂	168	57.3		
Cyclopentane, <i>c</i> -C ₅ H ₁₀	153	54.9	215	57.3
Hexane, <i>n</i> -C ₆ H ₁₄	192	65.7	239 ^c	61.3
Cyclohexane, <i>c</i> -C ₆ H ₁₂	167	60.1	228	60.9
Heptane, <i>n</i> -C ₇ H ₁₆	211	72.3	256 ^c	66.2
Cycloheptane, <i>c</i> -C ₇ H ₁₄	195	70.4	246	65.8
Octane, <i>n</i> -C ₈ H ₁₈	227	78.0	277 ^c	73.4
Cyclooctane, <i>c</i> -C ₈ H ₁₆	215	77.8	260	69.7
Nonane, <i>n</i> -C ₉ H ₂₀			286 ^c	74.2
Cyclononane, <i>c</i> -C ₉ H ₁₈				
Decane, <i>n</i> -C ₁₀ H ₂₂	272	93.8	297 ^c	76.6
Cyclodecane, <i>c</i> -C ₁₀ H ₂₀	252	91.5		

$\Delta E_{\text{des}}^\ddagger$ were calculated using Redhead analysis [18] of TPD data with $\beta = 2$ K/s.

^a Pre-exponential factors of $v = 10^{17.5}$ and $10^{18.5}$ s⁻¹ were used for linear and cyclic alkanes, respectively.

^b A pre-exponential factor of $v = 10^{13.4}$ s⁻¹ was used for cyclic alkanes. Pre-exponential factors used for linear alkanes are listed in Table 2.

^c From Bishop et al. [3].

with a value of the slope of $\Delta E_{\text{des}}^\ddagger/R$. Given the value of $\Delta E_{\text{des}}^\ddagger$ one can then determine the value of the desorption pre-exponential factor, v .

TPD experiments were conducted using variable heating rates in order to determine values of both $\Delta E_{\text{des}}^\ddagger$ and v for *n*-C₇H₁₆ desorption from the Cu(111) surface. Fig. 2 shows TPD spectra for *n*-C₇H₁₆ at monolayer coverage desorbing from Cu(111) during heating at rates varying from 0.1 to 2 K/s. To ensure a reproducible initial coverage of one monolayer, adsorption was performed with the Cu(111) sample held at a temperature just above the *n*-C₇H₁₆ multilayer desorption temperature. The spectra were generated by using the QMS to monitor the signal at $m/q = 43$ (C₃H₇⁺) during heating. The basic observation was that the monolayer peak desorption temperature increased as the heating rate was increased. The inset shows a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$. Values of $\Delta E_{\text{des}}^\ddagger = 73.4 \pm 4.5$ kJ/mol and $v = 10^{17.5 \pm 1.2}$ s⁻¹ were determined for *n*-C₇H₁₆ desorption from Cu(111).

Values of $\Delta E_{\text{des}}^\ddagger$ and v for *c*-C₇H₁₄ desorption from the Cu(111) surface were also determined

independently using the variable heating rate method. Fig. 3 shows TPD spectra of *c*-C₇H₁₄ at one monolayer coverage desorbing from the Cu(111) surface measured at heating rates ranging from 0.1 to 2 K/s. As before, the Cu(111) sample was held at a temperature just above the *c*-C₇H₁₄ multilayer desorption temperature to ensure adsorption of a reproducible coverage of one monolayer. Spectra were generated by monitoring the signal at $m/q = 41$ (C₃H₅⁺) during heating. As was the case for *n*-C₇H₁₆ desorption, the monolayer desorption temperature for *c*-C₇H₁₄ increased as the heating rate was increased. The inset shows a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ that was used to determine values of $\Delta E_{\text{des}}^\ddagger = 70.7 \pm 1.4$ kJ/mol and $v = 10^{18.5 \pm 0.4}$ s⁻¹ for *c*-C₇H₁₄ desorption from Cu(111).

Values of v for desorption of both linear and cyclic heptane from the Cu(111) surface are of order $v = 10^{18}$ s⁻¹. These are quite a high values but are consistent with values found for *n*-alkane desorption from the surface of graphite ($v = 10^{19.6}$ s⁻¹) in previous work [7,11,12]. We found that the

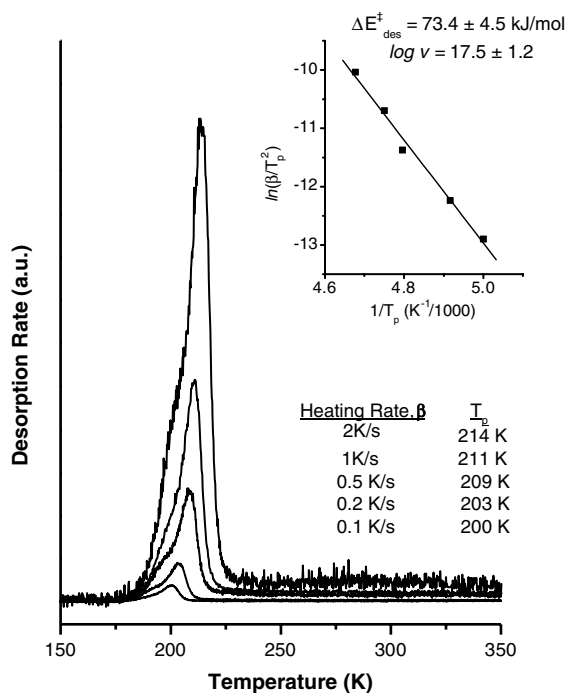


Fig. 2. TPD spectra of n -C₇H₁₆ desorbing from the Cu(111) surface measured for initial coverages of one monolayer at heating rates varying from $\beta = 0.1$ to 2 K/s. The inset is a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$. The slope of the linear fit has been used to estimate $\Delta E_{\text{des}}^{\ddagger}$ and v for n -C₇H₁₆ desorption. Spectra were generated by monitoring the signal at $m/q = 43$ (C₃H₇⁺) during heating.

pre-exponential factor for desorption was independent of chain length in our previous studies of the desorption of alkanes from the graphite surface and so we have chosen to use a value of $v = 10^{17.5} \text{ s}^{-1}$ for all linear alkanes and $v = 10^{18.5} \text{ s}^{-1}$ for all cyclic alkanes to evaluate $\Delta E_{\text{des}}^{\ddagger}$ from the Cu(111) surface.

3.3. $\Delta E_{\text{des}}^{\ddagger}$ of linear and cyclic alkanes from Cu(111) and Pt(111)

Values of $\Delta E_{\text{des}}^{\ddagger}$ for alkanes on Cu(111) and Pt(111) surfaces can be calculated using the Redhead equation and the peak desorption temperatures [18]. Peak temperatures for desorption of linear and cyclic alkanes from the two surfaces are listed in Table 1. Peak temperatures for desorption of linear alkanes from Pt(111) surfaces

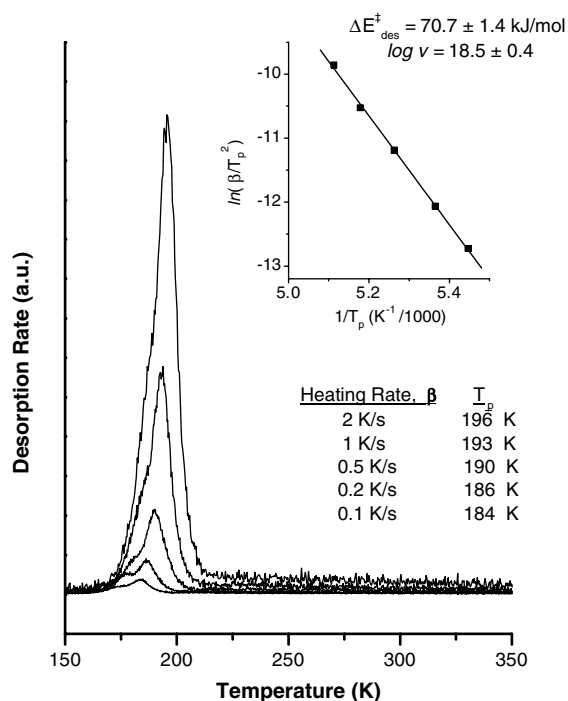


Fig. 3. TPD spectra of c -C₇H₁₄ desorbing from the Cu(111) surface measured for initial coverages of one monolayer at heating rates varying from $\beta = 0.1$ to 2 K/s. The inset is a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$. The slope of the linear fit has been used to estimate $\Delta E_{\text{des}}^{\ddagger}$ and v for c -C₇H₁₄ desorption. Spectra were generated by monitoring the signal at $m/q = 41$ (C₃H₅⁺) during heating.

were taken from the work of Bishop et al. [3] while the remainder come from this work. Values of $\Delta E_{\text{des}}^{\ddagger}$ from Cu(111) and Pt(111) surfaces were calculated using the Redhead equation. The choice of the pre-exponential factors that were used for analysis of the desorption kinetics from the Pt(111) surface will be discussed in the next section. Table 1 lists the values of $\Delta E_{\text{des}}^{\ddagger}$ for all the linear and cyclic alkanes studied on the Cu(111) and Pt(111) surfaces in this work and for the linear alkanes studied on Pt(111) by Bishop et al. [3]. Additional TPD measurements were made for the desorption of the cyclic alkanes from the (2×2) and (√3×√3)R30° Sn/Pt(111) alloys on Pt(111) surfaces. The values of $\Delta E_{\text{des}}^{\ddagger}$ were roughly 15% lower on the alloy surfaces than on the clean Pt(111) surface.

4. Discussion

Desorption kinetics for linear alkanes on Cu(111) and Pt(111) surfaces have been measured in this work and on the Au(111), Cu(100), Ru(001) surfaces and the basal plane of graphite in other work [1–8]. These data were used to estimate values of $\Delta E_{\text{des}}^{\ddagger}$ as a function of chain length. Table 2 lists these values and the values of $\log_{10}(v)$ that were used in the calculation of $\Delta E_{\text{des}}^{\ddagger}$. It is necessary to say some words regarding the choices of the values of v used for each surface because they have not been measured consistently among the studies published. In the case of the Au(111) surface, desorption rates for hexane through dodecane were measured isothermally and thus a value of v is not needed to estimate the values of $\Delta E_{\text{des}}^{\ddagger}$ [1]. Nonetheless the authors indicate that analysis of their isothermal data yielded values of $v = 10^{13} \text{ s}^{-1}$ that were independent of the alkane chain length. Furthermore, their TPD measurements yielded values of $\Delta E_{\text{des}}^{\ddagger}$ consistent with those measured isothermally. Bishop et al. [3] measured a value of $v \approx 10^{13} \text{ s}^{-1}$ for the desorption of three alkanes from the Pt(111) surface independent of the alkane chain length. Also, Weaver et al. [10] measured $v = 10^{13.8} \text{ s}^{-1}$ for the desorption of butane from the Pt(111) surface. Given these values, we have chosen to use $v = 10^{13.4} \text{ s}^{-1}$ to estimate the values of $\Delta E_{\text{des}}^{\ddagger}$ of *n*-butane and *n*-heptane on the Pt(111) surface using the TPD data of Xu et al. [19]. Paserba and Gellman [7] measured $v = 10^{19.6} \text{ s}^{-1}$ for a set of nine alkanes with chain lengths ranging from $N = 7$ to 44 adsorbed on graphite. In Table 2 we have listed the measured values of v and used $v = 10^{19.6} \text{ s}^{-1}$ for the alkanes for which v was not explicitly measured. Brand et al. [4] measured values of $v \approx 10^{16} \text{ s}^{-1}$ for four alkanes desorbing from the Ru(001) surface. This is the one instance in which the experimentally measured values of v decrease systematically with chain length. If one looks at the entire set of experimental data obtained from all surfaces, however, it appears that the value of v is not dependent on chain length. We have measured $v = 10^{17.5} \text{ s}^{-1}$ for *n*-C₇H₁₆ desorption from the Cu(111) surface and have used this value to calculate the values of $\Delta E_{\text{des}}^{\ddagger}$ for the other linear alkanes. On the Cu(100) sur-

face there have been no attempts to measure the value of v for alkane desorption and so we have used a value of $v = 10^{16} \text{ s}^{-1}$ in which the exponent is roughly the average of the values of $\log_{10}(v)$ obtained from all other studies. Although it is somewhat unsatisfying that the values of v have not been measured for the desorption of all of the alkanes on all of the surfaces, it should be pointed out that the values of $\Delta E_{\text{des}}^{\ddagger}$ obtained from the Redhead equation are only weakly dependent on the value of v . Increasing v by one order of magnitude only increases the value of the $\Delta E_{\text{des}}^{\ddagger}$ by $\sim 5\%$. From the perspective of this work, the possible errors in the values of $\Delta E_{\text{des}}^{\ddagger}$ arising from errors in the values of v are of no consequence. Even if all of the data were reanalyzed using a single value of 10^{16} s^{-1} , one would still find significant value of, ΔE , the intercept of the $\Delta E_{\text{des}}^{\ddagger}$ versus chain length plot and the basic point of this paper would not change.

Values of $\Delta E_{\text{des}}^{\ddagger}$ of cyclic alkanes from the Cu(111) and Pt(111) surfaces are also listed in Table 1. The only measurement of the value of v for desorption of cyclic alkanes was made for *c*-C₇H₁₄ on the Cu(111) surface and is reported in this work to be $v = 10^{18.5} \text{ s}^{-1}$. This value was used to estimate $\Delta E_{\text{des}}^{\ddagger}$ for all of the cyclic alkanes desorbing from the Cu(111) surface. The values of v are quite similar for desorption of the linear and the cyclic alkanes from the Cu(111) surface so, we assumed that the same is true for desorption from the Pt(111) surface and used a value of $v = 10^{13} \text{ s}^{-1}$ to estimate the values of $\Delta E_{\text{des}}^{\ddagger}$ for the desorption of the cyclic alkanes. In looking at Table 1, which compares $\Delta E_{\text{des}}^{\ddagger}$ on the Cu(111) and Pt(111) surfaces there appears to be no significant difference between the values of $\Delta E_{\text{des}}^{\ddagger}$ for the linear and the cyclic alkanes.

The aim of this work was to highlight the non-zero intercept of the correlation of $\Delta E_{\text{des}}^{\ddagger}$ with chain length, N . The data plotted in Fig. 4 clearly reveal that $\Delta E_{\text{des}}^{\ddagger}$ of alkanes varies linearly with chain length on all surfaces over short ranges of chain lengths. These values are not, however, proportional to chain length and the value of the intercept, ΔE , is significant in all cases. The Pt(111) surface is the only one for which $\Delta E_{\text{des}}^{\ddagger}$ of the linear alkanes is non-linear in chain length for

Table 2
Kinetic parameters for linear alkane desorption from surfaces

	Au(1 1 1) ^a [1]	Au(1 1 1) [9]	Cu(1 0 0) ^b [8]	Cu(1 0 0) ^b [2]	Cu(1 1 1) ^c [this paper]	Pt(1 1 1) [10]	Pt(1 1 1) ^d [3]	Pt(1 1 1) ^e [this paper]	Graphite ^f [7]	Ru(0 0 1) [4]
Method	He Scatt., TPD	MD	TPD	TPD	TPD	TPD	TPD	TPD	TPD	TPD
Heating rate, β	Iso T	Iso T	3	5	2	4	2	4	2	0.03–15
<i>n</i> -C ₃ H ₈					40.2, 17.5 ^g					46, 16.5
<i>n</i> -C ₄ H ₁₀	40.5, 13 ^g	40, 13.6		46.3, 16 ^g		50.6, 13.8		46.5, 13.4 ^g		49.8, 15.6
<i>n</i> -C ₅ H ₁₂			53.3, 16 ^g	53.5, 16 ^g	57.3, 17.5 ^g				65.0, 19.6 ^g	57.7, 15.3
<i>n</i> -C ₆ H ₁₄	55.9, 13	62, 14.6	60.9, 16 ^g	62.0, 16 ^g	65.7, 17.5 ^g		61.3, 12.8		73.6, 19.6 ^g	62.7, 14.9
<i>n</i> -C ₇ H ₁₆	62.7, 13			69.9, 16 ^g	72.4, 17.5		66.2, 12.9 ^g	68.5, 13.4 ^g	78.2, 18.8	
<i>n</i> -C ₈ H ₁₈	69.7, 13	82, 15.4		74.6, 16 ^g	78.0, 17.5 ^g		73.4, 13.2		88.2, 19.6 ^g	
<i>n</i> -C ₉ H ₂₀	75.2, 13			82.9, 16 ^g			74.2, 12.9 ^g			
<i>n</i> -C ₁₀ H ₂₂	80.1, 13	98, 16.0		91.5, 16 ^g	93.8, 17.5 ^g		76.6, 12.8		101, 19.6 ^g	
<i>n</i> -C ₁₁ H ₂₄										
<i>n</i> -C ₁₂ H ₂₆	93.6, 13	121, 16.4							119, 20.3	

Each entry contains values of $[\Delta E_{\text{des}}^{\ddagger}, \log_{10}(v)]$.

^a Values of v were determined from intercepts of Arrhenius plots of isothermal desorption rates.

^b Values of v were estimated from the average of values of $\log_{10}(v)$ obtained on other surfaces.

^c Value of v was measured for *n*-C₇H₁₆ and this value was used for all other linear alkanes on the Cu(1 1 1) surface.

^d Values of v for *n*-C₇H₁₆ and *n*-C₉H₂₀ were estimated from the average value of $\log_{10}(v)$ obtained for other linear alkanes in this study.

^e Value of v was estimated from the average of the values of $\log_{10}(v)$ found in the other two studies on the Pt(1 1 1) surface [3,10].

^f The value of $\log_{10}(v) = 19.6$ is the average of values determined for alkanes with chain lengths in the range $N = 7-44$ [7].

^g Values of v were not measured and have been estimated as described in the text.

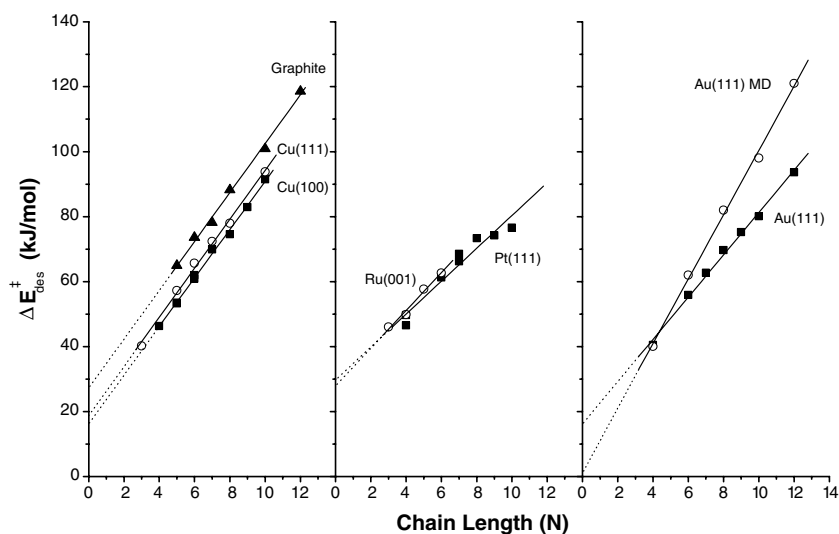


Fig. 4. $\Delta E_{\text{des}}^{\ddagger}$ for linear alkane desorption from surfaces as a function of chain length, N . The lines are linear fits for each surface and reveal the significant values of the intercept, ΔE .

$N < 12$. Nonetheless, even if one analyzes only the shorter linear alkanes on the Pt(111) surface a linear correlation of the $\Delta E_{\text{des}}^{\ddagger}$ with chain length would yield a significant value for ΔE . It is interesting that a united atom model used as the basis for a molecular dynamics study of alkane desorption from the Au(111) surface, predicts values of $\Delta E_{\text{des}}^{\ddagger}$ that are proportional to the chain length and thus yield a value of $\Delta E \approx 0$ [9]. Thus the origin of the experimentally observed magnitude of ΔE is worth examining.

Table 3 lists values of the parameters used in linear fits of $\Delta E_{\text{des}}^{\ddagger}$ versus N . Values of ΔE vary in magnitude from 2 to 6 times the value of the segmental increment, ΔE^{CH} , to $\Delta E_{\text{des}}^{\ddagger}$. The physical origin of ΔE is unclear and it is hard to see how it could arise from a description of the adsorbate–substrate interaction that is simply composed of pairwise additive contributions between adsorbate segments and the surface. New data that we have presented in this paper eliminate a couple of the possible factors that might contribute to the value of ΔE .

4.1. Endgroup effects

The simplest model for the interaction between an alkane and a surface would be one in which the

Table 3

Segmental increment, ΔE^{CH} , and intercepts for zero chain length, ΔE , for the $\Delta E_{\text{des}}^{\ddagger}$ of linear and cyclic alkanes adsorbed on a number of surfaces

Surface/alkanes	ΔE^{CH} (kJ/mol/CH ₂)	ΔE (kJ/mol)
Pt(111)/ n -C _N H _{2N+2}	5.0	30.0
Ru(001)/ n -C _N H _{2N+2}	5.8	28.0
Au(111)/ n -C _N H _{2N+2}	6.5	16.2
Cu(100)/ n -C _N H _{2N+2}	7.4	16.6
Cu(111)/ n -C _N H _{2N+2}	7.5	19.0
Graphite/ n -C _N H _{2N+2}	7.5 (6.2)	27.2 (41)
Au(111)/ n -C _N H _{2N+2} (MD)	9.9	1.4
Pt(111)/ c -C _N H _{2N}	4.2	36.0
Cu(111)/ c -C _N H _{2N}	7.2	19

alkane is thought of as a chain of identical segments that each interact with the surface with the same potential. This type of model has often been used to describe alkanes and hydrocarbons adsorbed on surfaces. This type of model must break down for short chains because methyl endgroups cannot be equivalent to the internal methylene groups. While the effects of endgroups on $\Delta E_{\text{des}}^{\ddagger}$ might be negligible for long chains, their relative contribution to $\Delta E_{\text{des}}^{\ddagger}$ must increase as the chain length decreases. This would manifest itself in the form of an offset to the $\Delta E_{\text{des}}^{\ddagger}$ or a non-zero intercept, ΔE , of the type observed in this work.

The values of ΔE for the linear alkanes vary from 16.6 to 30.0 kJ/mol among the different surfaces on which they have been studied while the segmental increments, $\Delta E^{\ddagger}_{\text{des}}$, to the $\Delta E^{\ddagger}_{\text{des}}$ vary from 5.0 to 7.5 kJ/mol. This suggests that endgroup effects cannot account for the observed values of ΔE because the magnitudes of the values of ΔE suggest that they cannot arise simply from the differences between the interactions of methylene and methyl groups with the surface. Nonetheless, this work has attempted to address this possibility specifically by comparing $\Delta E^{\ddagger}_{\text{des}}$ of linear alkanes with those of cyclic alkanes on both Cu(111) and Pt(111) surfaces. Fig. 5 shows a plot of $\Delta E^{\ddagger}_{\text{des}}$ versus N for cyclic alkanes on both Cu(111) and Pt(111) surfaces. Fits to straight lines are shown and fitting parameters are given in Table 3. On both surfaces, the values of ΔE are similar for both linear and cyclic alkanes. This

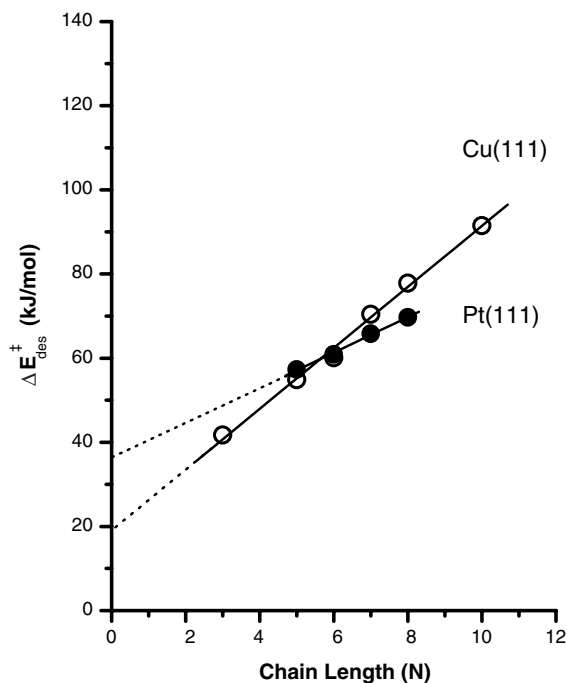


Fig. 5. $\Delta E^{\ddagger}_{\text{des}}$ for cyclic alkane desorption from Cu(111) and Pt(111) surfaces as a function of chain length, N . The lines are linear fits for each surface and reveal the significant values of the intercept, ΔE . These values are similar to those of the linear alkanes.

suggests that ΔE arises from an intrinsic property of the surface rather than the alkanes. More importantly, ΔE for cyclic alkanes cannot arise from endgroup effects since they have no endgroups. Nonetheless the values of ΔE on both surfaces are significant. TPD data obtained from the (2×2) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sn/Pt(111) alloys on Pt(111) surfaces also show that the correlations of $\Delta E^{\ddagger}_{\text{des}}$ with chain length reveal significant values of ΔE . Table 1 shows that linear alkanes have values of $\Delta E^{\ddagger}_{\text{des}}$ that are ~ 2 kJ/mol higher than those of the cyclic alkanes on both the Cu(111) and Pt(111) surfaces. This suggests that the interactions of methyl groups with these surfaces are about 1 kJ/mol greater than those of methylene groups. This seems to be of a reasonable magnitude and certainly indicates that the observed magnitude of ΔE cannot be attributed to endgroup effects.

4.2. Physical properties of alkanes with varying chain length

Many properties of linear alkanes are chain length dependent and their correlation with chain length might provide some insight into the origins of ΔE . One such property is the heat of vaporization, ΔH_{vap} , which arises principally from the interactions between alkanes in the bulk. A correlation between ΔH_{vap} and chain length should also reveal endgroup effects, in much the same way as one would expect to observe them in the correlation of $\Delta E^{\ddagger}_{\text{des}}$ with chain length. Fig. 6 shows a plot of ΔH_{vap} versus N for n -alkanes ranging in length from $N = 1$ to 12 [20]. Values reported for butane and higher alkanes are all reported for 273 K. ΔH_{vap} is linear in the chain length with fitting parameters of $\Delta H^{\text{CH}} = 4.9$ kJ/mol and $\Delta H = 2.4$ kJ/mol. The value of the segmental increment to ΔH_{vap} is slightly lower than that of $\Delta E^{\ddagger}_{\text{des}}$ on most surfaces. The magnitude of $\frac{1}{2}\Delta H = 1.2$ kJ/mol is significantly smaller than the segmental increment in ΔH_{vap} and this value might reasonably be attributed to the excess contribution of a methyl endgroup to ΔH_{vap} . Furthermore, a value of 1.2 kJ/mol is similar to the endgroup effects on $\Delta E^{\ddagger}_{\text{des}}$ reported in this work. The value of ΔH is, however, much smaller than the values of ΔE measured

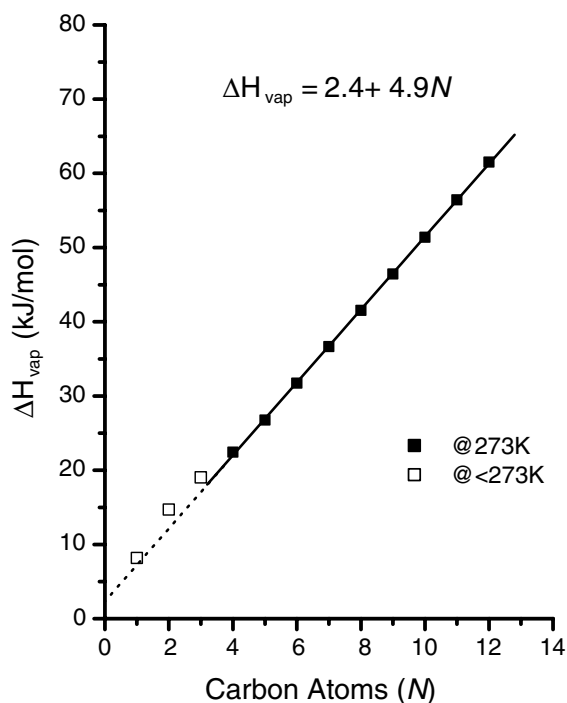


Fig. 6. Correlation of the heat of vaporization, ΔH_{vap} , for the linear alkanes with chain length, N . The straight line is a fit to the values of ΔH_{vap} for the alkanes with $N \geq 4$ and yields an intercept ΔH that is smaller than the increment to ΔH_{vap} per methylene group.

for desorption of the alkanes from surfaces and provides us with little insight into the origin of ΔE .

4.3. Polarizability effects

Polarizability, α , is another property of alkanes that scales with chain length. Furthermore, the magnitude of the alkane–surface interaction should be correlated with the polarizability of the alkanes because it occurs through weak van der Waals forces. As such the chain length dependence of the polarizability might account for the chain length dependence of $\Delta E_{\text{des}}^{\ddagger}$ and thus the magnitude of ΔE . The correlation between values of $\Delta E_{\text{des}}^{\ddagger}$ and α is illustrated in Fig. 7. Once again there is a significant value of the intercept, ΔE , for both the linear and cyclic alkanes on both surfaces. Polarizability can be described well as a group-additive property and polarizabilities of alkanes are almost proportional to chain length [21,22]. As

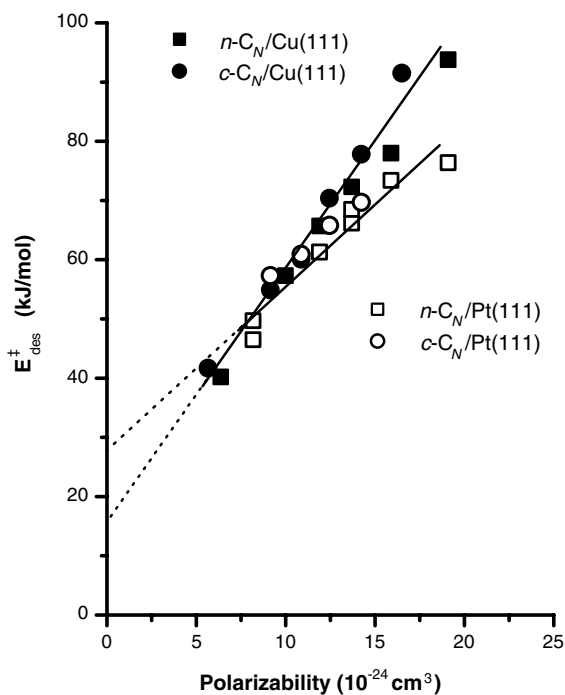


Fig. 7. Correlation of the $\Delta E_{\text{des}}^{\ddagger}$ for linear and cyclic alkane desorption from the Cu(111) and Pt(111) surfaces with alkane polarizability. Both correlations yield significant values of the intercept, ΔE .

a consequence, the chain length dependence of polarizabilities cannot account for the non-zero value of ΔE .

4.4. Temperature effects

The nature of the thermal desorption experiment is such that the adsorbate desorbs from the surface in a narrow temperature range around a peak desorption temperature that is dictated in part by the $\Delta E_{\text{des}}^{\ddagger}$. As a consequence, the desorption kinetics of a set of linear or cyclic alkanes are all measured at different temperatures. Even in an isothermal measurement, the temperature used to make the measurement will depend on the length of the alkane since desorption must occur at a significant rate to be measurable. The fact that the desorption measurements have been made at different temperatures for the different alkanes might, in principle, introduce an artifact into the measured values of $\Delta E_{\text{des}}^{\ddagger}$ that could be manifested in

the form a non-zero intercept, ΔE . This issue has been addressed in a prior study of linear alkane desorption from the surface of graphite [7,11,12]. That study included linear alkanes ranging in length from $N = 5$ to 60 which desorbed from the surface at temperatures ranging from $T_p = 180$ to 730 K. Those measurements revealed that $\Delta E_{\text{des}}^\ddagger$ is non-linear in the chain length. A theory was developed that provides an expression that accurately reproduced the measured values of $\Delta E_{\text{des}}^\ddagger$:

$$\Delta E_{\text{des}}^\ddagger = (N - 1) \cdot \left[\frac{q^{\text{tg}} \cdot \Delta E^{\text{CC}} + (q^{\text{tg}} - 1) \cdot \Delta E_{\text{tg}}^{\text{CC}}}{q^{\text{tg}} \left(1 + q^{\text{tg}} \cdot \exp \left(\frac{-\Delta E^{\text{CC}}}{k_B T} \right) \right)} \right] + \Delta E + k_B T. \quad (2)$$

In this expression q^{tg} is the *trans-gauche* partition function for each C–C bond, as given by

$$q^{\text{tg}} = 1 + 2 \cdot \exp \left(\frac{-\Delta E_{\text{tg}}^{\text{CC}}}{k_B T} \right), \quad (3)$$

where $\Delta E_{\text{tg}}^{\text{CC}}$ is the energy difference between the *trans* and *gauche* conformations about each C–C bond. The only two unknown parameters in the expression for $\Delta E_{\text{des}}^\ddagger$ are ΔE^{CC} , the bond–surface interaction energy, and ΔE . These were found by fitting to the experimentally determined values of $\Delta E_{\text{des}}^\ddagger$ for linear alkanes on graphite. The values of these fitting parameters found for desorption of linear alkanes from graphite are listed in parentheses in row 4 of Table 3. While Eq. (2) accurately reproduces the non-linearity of $\Delta E_{\text{des}}^\ddagger$ obtained from measurements made over a wide range of temperatures (170–720 K) and using a wide range of chain lengths ($N = 5$ –60) it cannot do so without ΔE taking on a significant value of 41 kJ/mol. In other words, the correct inclusion of temperature effects into the expression for the $\Delta E_{\text{des}}^\ddagger$ for linear alkanes desorbing from graphite does not eliminate the need for a significant value of ΔE .

4.5. Order of the desorption reaction

Our analysis of the kinetics of desorption of alkanes from Cu(1 1 1) and Pt(1 1 1) surfaces, and

all other analyses in previously reported studies have assumed that the desorption is first-order in coverage, i.e. it is directly proportional to the alkane coverage on the surface. In the case of desorption of alkanes from the Cu(1 1 1) surface, this is supported by the observation that the peak desorption temperature is independent of coverage. On other surfaces, however, the shape of the desorption peaks is not entirely consistent with that of a simple first-order process. For example, the desorption of the short *n*-alkanes from Pt(1 1 1) and graphite surfaces exhibits peaks with shapes that are similar to those that one would expect for a zero-order desorption process [3,7]. Desorption mechanisms that manifest zero-order desorption kinetics have been proposed to involve desorption from a 2D gas in equilibrium with a 2D condensed phase. It is possible that this occurs during alkane desorption. Alternately, kinetics that are apparently zero-order can arise from a first-order desorption process coupled with attractive interactions between adsorbed species. In any case, Bishop et al. [3] suggested that the origin of the non-zero value of ΔE may arise from incorrect analysis of the desorption kinetics using a first-order rate equation when the kinetic order of the desorption process may be changing with chain length. Isothermal measurements of the desorption of alkanes from the Au(1 1 1) surface, however, yielded results that were consistent with a first-order desorption process and suggest that this is the case for all alkanes ranging in length from $N = 1$ to 12 [1]. Nonetheless, it is worthwhile considering explicitly the influence of reaction order on the values of $\Delta E_{\text{des}}^\ddagger$ determined by analysis of TPD measurements.

In order to probe the sensitivity of the data analysis to the kinetic order of the desorption process, we have simulated the TPD spectra using a desorption rate expression of the form

$$r = -\frac{d\theta}{dt} = k \cdot \theta^n, \quad (4)$$

where θ is the coverage, k is an Arrhenius-like rate constant, and n is the order of the desorption process. Simulated desorption spectra are shown in Fig. 8 for a rate constant with a pre-exponential factor of $\nu = 10^{13} \text{ s}^{-1}$ and a desorption barrier of $\Delta E_{\text{des}}^\ddagger = 20 \text{ kJ/mol}$. The peak desorption tempera-

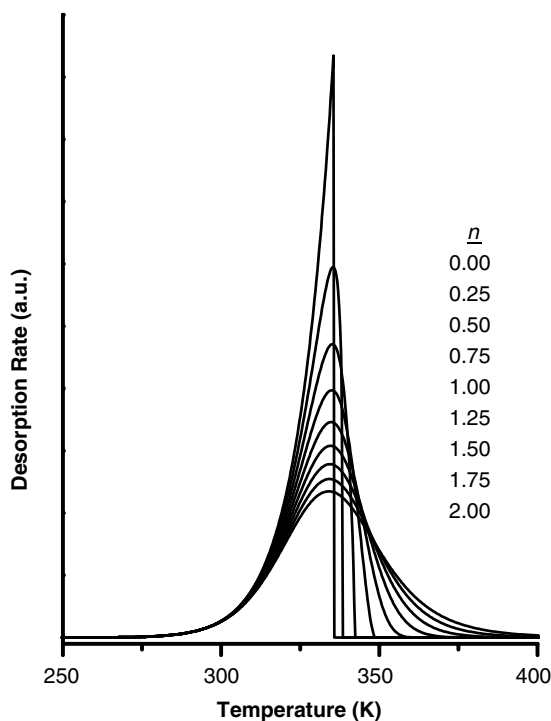


Fig. 8. Simulations of TPD spectra for reaction orders varying from $n = 0$ to 2. The Arrhenius rate constant used a pre-exponential factor of $\nu = 10^{13} \text{ s}^{-1}$ and a desorption energy of $\Delta E_{\text{des}}^{\ddagger} = 20 \text{ kJ/mol}$. Note that the peak desorption temperature, T_p , is insensitive to the order of the desorption process.

ture, T_p , was determined from these simulations for values of n ranging from 0 to 2. The result is that $T_p \approx 335 \text{ K}$ is virtually independent of the reaction order, varying by less than 1% throughout the range of kinetic orders from $n = 0$ to 2. Since the analysis of TPD spectra to determine $\Delta E_{\text{des}}^{\ddagger}$ from the first-order desorption equation relies only on T_p , any error in the assumed reaction order introduces a negligible error into the estimate for $\Delta E_{\text{des}}^{\ddagger}$. Thus, possible chain length-dependent changes in the order of the alkane desorption process cannot account for the magnitude of ΔE .

A further point should be made with regard to the possible role of reaction order in the value of ΔE . ΔE is significant even for the desorption of alkanes with lengths as high as $N = 60$ adsorbed on graphite. The desorption kinetics of alkanes over this wide range of chain lengths still manifest a non-zero value of ΔE even if the data are ana-

lyzed only for long chains in the length range $N = 20\text{--}60$. Although TPD spectra for short chain alkanes appear to have a shape indicative of a zero-order desorption process, the TPD spectra for the longer chain alkanes can all be fit quite well using a first-order desorption rate equation. Moreover, it is not likely that the order of the desorption process would change over a range of $N = 20\text{--}60$. In summary, it seems unlikely that ΔE can arise from an unknown error in the order of the desorption process used to analyze alkane desorption kinetics from surfaces.

4.6. Commensurability

As a final consideration in our discussion of the origin of ΔE , we address the influence of commensurability of the substrate lattice and the natural periodicity of alkane chains. If one imagines two rigid periodic arrays in contact, then it is quite clear that the interaction will depend on the mismatch of the lattice spacings of the two arrays. Fig. 9A illustrates the case in which an alkane and substrate have the same periodicity and all the carbon atoms sit in potential minima at the surface. If there is lattice mismatch, then the minimum energy configuration (Fig. 9B) is a complicated function of the chain periodicity and shape of the potential. It is only in the extreme case of Fig. 9C, in which the interaction potential is flat with extremely narrow, periodic minima, that the desorption energy could have the form

$$\Delta E_{\text{des}}^{\ddagger}(N) = \Delta E + \Delta E^{\text{CH}} \cdot N. \quad (5)$$

This form of the potential for the interaction of the alkanes with any of the surfaces seems physically unrealistic. MD simulations of the adsorption of the alkanes on Au(111) surfaces and Pt(111) surfaces have used a united atom model for the alkanes and a realistic potential for their interaction with the surfaces. These simulations show no evidence of commensurability issues and predict that the minimum binding energy of the alkanes in the all-*trans* configuration is proportional to the chain length [9,23]. If commensurability issues were important, they would be expected to appear in such simulations of Au(111) and Pt(111) surfaces but disappear on a surface such as that of

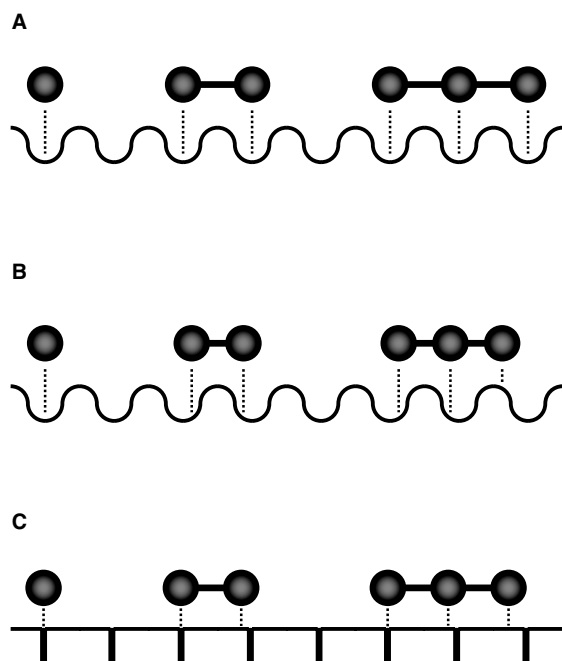


Fig. 9. Illustrations of the interaction of alkanes of lengths $N = 1$ to 3 with three periodic potential energy surfaces. (A) The alkane and the surface have the same periodicity and are commensurate. The total interaction energy ought to be proportional to the alkane chain length leading to $\Delta E_{\text{des}}^{\ddagger}(N) = N \cdot \Delta E^{\text{CH}}$. (B) The alkane and the surface have different periodicities and are incommensurate. The total interaction energy is a complex, non-linear function of the chain length. (C) The alkane and the surface have different periodicities and the interaction potential with the surface is uniform but with periodic, sharp minima. The interaction of the alkanes with this type of surface would lead to a desorption energy of the form $\Delta E_{\text{des}}^{\ddagger}(N) = \Delta E + N \cdot \Delta E^{\text{CH}}$.

graphite which is closely lattice matched to the alkanes. In fact, they do not appear in simulations on Au(111) and Pt(111) surfaces while the experimentally measured value of ΔE is significant on the graphite surface.

A second compelling argument against lattice commensurability giving rise to ΔE comes from comparison of $\Delta E_{\text{des}}^{\ddagger}$ for the linear and cyclic alkanes. Although both have similar C–C bond lengths, the geometry of cyclic alkanes is highly constrained and it seems unlikely that their registry with various substrate lattices could be similar to that of the linear alkanes. Inspection of the results in Table 3, however, reveals that linear and

cyclic alkanes have similar values of ΔE on the Cu(111) surface. The same is true of the values of ΔE on the Pt(111) surface. Furthermore, values of ΔE^{CH} for the linear and cyclic alkanes are similar on Cu(111) and Pt(111) surfaces. It is also rather interesting that the constrained geometries of the cyclic alkanes of different lengths do not perturb the linear dependence of $\Delta E_{\text{des}}^{\ddagger}$ on chain length. Our conclusion from these considerations is that lattice commensurability is not the primary origin of ΔE .

4.7. Chain length dependence of the pre-exponential factor

Perhaps the least well determined parameter in our description of the kinetics of alkane desorption from surfaces is the pre-exponential factor of the desorption rate constant. Isothermal measurements by Wetterer et al. [1] yielded a value of $\nu = 10^{13} \text{ s}^{-1}$ from the intercepts of Arrhenius plots of the desorption rate constants for hexane through dodecane. Several TPD studies have used variable heating rate measurements to measure values ranging from $\nu = 10^{13}$ to 10^{19} s^{-1} . In analyzing the data presented in Table 2, we have attempted to estimate the pre-exponential factors for alkane desorption from each of the surfaces. Values of ν and the $\Delta E_{\text{des}}^{\ddagger}$ compensate for one another in analysis of desorption kinetics such that an error of one order of magnitude in ν corresponds to an error of roughly 5% in the value of $\Delta E_{\text{des}}^{\ddagger}$. It is also important to point out that if one reanalyzed all of the experimental data by simply assuming that pre-exponential factors always have a value of $\nu = 10^{13} \text{ s}^{-1}$, one would still find that $\Delta E_{\text{des}}^{\ddagger}$ scales linearly with alkane length in such a way that the intercept, ΔE , is significant. In other words the anomaly that is the focus of this paper does not disappear simply by assuming that the pre-exponential factor is always $\nu = 10^{13} \text{ s}^{-1}$.

Molecular dynamics simulation of alkane desorption from surfaces has been used recently to determine the predictions of a united atom model of the alkane–Au(111) interaction [9]. The results of that work are compared directly to the experimental data of Wetterer et al. [1]. As one would imagine, adsorption energies, ΔE_{ads} , of the all-

trans configurations of linear alkanes on the Au(111) surface are predicted to be proportional to the chain length. On the other hand, values of $\Delta E_{\text{des}}^{\ddagger}$ determined from transition state theory analysis of the simulated desorption rates vary non-linearly with chain length and fall below the energies of the all-*trans* minimum energy configurations. This is a direct result of the fact that the alkanes at elevated temperatures can adopt a number of configurations with energies above those of the global minimum energy configuration. These configurations represent a distribution of states from which desorption occurs and thus yield values of $\Delta E_{\text{des}}^{\ddagger}$ that are lower than the values of the adsorption energies, ΔE_{ads} . This is the same conclusion as was reached in the analysis of alkane desorption from graphite surfaces although the model used for the alkane–graphite interaction [12] was much more primitive than the united atom model used to simulate the alkane–Au(111) interaction [9].

The molecular dynamics simulations of alkane desorption from the Au(111) surface also predict values of the desorption pre-exponential factors. These values increase with increasing chain length from $v = 10^{12.2} \text{ s}^{-1}$ for methane to $v = 10^{16.4} \text{ s}^{-1}$ for *n*-C₁₂H₂₆. The much simpler model used to analyze the desorption of alkanes from graphite also predicts that the desorption pre-exponents should increase with chain length for alkanes with less than 20 carbon atoms [12]. Wetterer et al. [1], on the other hand, report that their Arrhenius plots of alkane desorption rates from the Au(111) surface yield values of $v \approx 10^{13} \text{ s}^{-1}$ that are independent of chain length. The interesting thing is that Fichtorn and Miron [9] show that the values of T_p predicted using their values of v and $\Delta E_{\text{des}}^{\ddagger}$ are almost identical to those that would be predicted by Wetterer et al. [1] using their values of $\Delta E_{\text{des}}^{\ddagger}$ and $v \approx 10^{13} \text{ s}^{-1}$. Fundamentally, this arises from the coupling between v and $\Delta E_{\text{des}}^{\ddagger}$ in the equations used to analyze desorption kinetics. These results suggest that analysis of desorption measurements assuming a constant value of v biases the values of $\Delta E_{\text{des}}^{\ddagger}$ incorrectly. If one analyzed desorption spectra using values of v that increased with chain length, then one would find values of $\Delta E_{\text{des}}^{\ddagger}$ that are proportional to chain length (over short ranges of

the chain length) and do not exhibit the intercept, ΔE . Thus, it is possible that the origin of ΔE lies in a poor determination of the values of v and the incorrect assumption that it is independent of alkane chain length.

There are several important differences between the model used for molecular dynamics model of alkane desorption from the Au(111) surface and the conditions of experimental studies. Perhaps the most important one is coverage. The simulations are done for single molecules adsorbed on a Au(111) surface and thus neglect intermolecular interactions while the experiments are often done at coverages approaching a monolayer at which intermolecular interactions may be significant. Experimental studies of alkane desorption that have used varying coverages have indicated that desorption is a first-order process and that the desorption energetics are independent of coverage. There has been no attempt, however, to examine the effects of coverage on the desorption pre-exponential factor.

A puzzling aspect of the experimental results is that most indicate that the desorption pre-exponential factor is independent of chain length [3,7,11,12]. As mentioned, Wetterer et al. [1] report that the intercepts of their Arrhenius plots indicate a value of $v \approx 10^{13} \text{ s}^{-1}$ that is independent of chain length. The exception is the study of alkane desorption from the Ru(001) surface which showed that the pre-exponential factor decreased with increasing chain length [4]. In contrast, models for alkane desorption from both Au(111) and graphite indicate that the pre-exponent should increase with increasing chain length at least for short chain lengths ($N < 20$) [9,12]. Thus, although errors in the desorption pre-exponential factor could serve to explain the origin of ΔE there is no experimental evidence from data obtained on metal surfaces to suggest that the desorption pre-exponential factor increases with chain length. It should be pointed out, however, that a recently reported set of data for the desorption of straight chain alkanes from MgO does show this increase of the pre-exponential factor with chain length [24]. Further analysis of alkane desorption kinetics to yield meaningful pre-exponential factors is necessary to fully understand this problem.

5. Conclusion

Our comparison of the desorption kinetics of linear and cyclic alkanes from Cu(111) and Pt(111) surfaces revealed a phenomenological dependence of the desorption energy on chain length, N , that has the form $\Delta E_{\text{des}}^{\ddagger}(N) = \Delta E + \Delta E^{\text{CH}} \cdot N$ and is consistent with data obtained for linear alkane desorption from many other surfaces. The origin of ΔE is puzzling, but our comparison of desorption of linear and cyclic alkanes categorically rules out any significant endgroup effects or commensurability effects. Unfortunately, our consideration of a number of other possible origins of ΔE has shed little light on this problem. The appearance of ΔE in studies of alkane desorption from surfaces is ubiquitous. Of the possible origins of ΔE , the most plausible seems to be the possibility of errors in the values of the desorption pre-exponential factors used to analyze the desorption data. Molecular dynamics simulations predict that desorption pre-exponential factors should increase with chain length and the physical arguments for this are reasonable. This could eliminate the intercept ΔE found by analysis of TPD data, however, there is no experimental evidence for an increase of the desorption pre-exponential factor with chain length. At this point in time, the origin of ΔE remains a mystery.

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