C–H Bond Activation of Light Alkanes on Pt(111): Dissociative Sticking Coefficients, Evans–Polanyi Relation, and Gas–Surface Energy Transfer†

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Received: May 14, 2010; Revised Manuscript Received: July 9, 2010

Effusive molecular beam experiments were used to measure alkane dissociative sticking coefficients, \( S(T_g, T_s) \), for which the impinging gas temperature, \( T_g \), and surface temperature, \( T_s \), could be independently varied. The 400—1000 K temperature range examined should be relevant to heterogeneous catalyzed industrial processes such as the steam reforming of alkanes. Methane, ethane, and propane all showed increasing dissociative sticking as either \( T_g \) or \( T_s \) were increased—indicative of an activated reaction mechanism. Effusive beam experiments with gas impinging along the surface normal and \( T_g = T_s = T \) determined \( S_0(T) \), a close approximation and formal upper bound to the thermal dissociative sticking coefficient, \( S(T) \), appropriate to reaction with a thermal ambient gas. Activation energies determined from \( S_0(T) \) for methane, ethane, and propane are \( E_a = 58, 43, \) and 34 kJ mol\(^{-1}\), respectively. An Evans–Polanyi plot of \( E_a \) for alkane dissociative chemisorption versus the alkane thermal desorption energy, \( E_D \), is linear with a slope of \(-0.94\). Assuming that the alkane \( E_a \) serves as a good approximation to the van der Waals stabilization of the chemisorbed alkyl radical product of dissociative chemisorption, the slope of the Evans–Polanyi plot indicates a late transition state for alkane dissociative chemisorption on Pt(111). A microcanonical unimolecular rate theory (MURT) model of dissociative chemisorption was used to analyze the effusive molecular beam experiments. Explicit accounting of the gas–surface energy transfer for the nonequilibrium experiments became increasingly important as the alkane size was increased. A simple exponential down model of the molecule/phonon collision step size distribution with a mean energy down parameter of \( \alpha = 350 \) cm\(^{-1}\) for ethane, and \( \alpha = 1400 \) cm\(^{-1}\) for propane, sufficed to provide a good description of the \( S_0(T_g, T_s) \) data. The methane \( S_0(T_g, T_s) \) values reported here for effusive molecular beams are roughly 2.5 times smaller than expectations based on MURT analysis of earlier, higher energy, supersonic molecular beam experiments.

1. Introduction

Light alkanes are abundant small molecules found in natural gas, and through their conversion to synthesis gas (a mixture of CO and H\(_2\)) and olefins they provide some of the essential feedstocks for the chemical industry. Consequently, C–H bond activation of alkanes has remained a topic of considerable practical and fundamental interest.\(^1\) Although activated dissociative chemisorption of molecules at surfaces is often considered to be the rate determining step in heterogeneous catalytic processes,\(^2\) there is only a modest experimental database of information about dissociative sticking.\(^3\) Kinetics studies by Wei and Igelsia\(^4^,\)\(^5\) have shown that methane reforming over supported metal nanocatalysts, at temperatures near 873 K and 1 bar pressure, is rate limited by methane dissociative chemisorption. Interestingly, although methane reforming is a structure sensitive process,\(^4^,\)\(^5\) surface science studies find that thermal dissociative sticking coefficients for methane on flat metal surfaces are several orders of magnitude higher than apparent values derived from reforming turnover rates on metal nanocatalysts.\(^6^–\)\(^8\) In this paper, we report dissociative sticking coefficients, \( S_0(T_g, T_s) \), for the activated dissociative chemisorption of methane, ethane, and propane on Pt(111). A normally incident effusive molecular beam was used to dose the alkanes onto the surface and postreaction Auger electron spectroscopy was used to monitor the carbon of the chemisorbed alkyl radical reaction product. Effusive molecular beams allowed the alkane reactivity to be investigated under (i) quasi-thermal equilibrium conditions comparable to those found in industrial catalysis, and (ii) nonequilibrium conditions where gas–surface energy transfer was intimately linked to reactivity.

Activated dissociative chemisorption kinetics for molecules that desorb from surfaces at temperatures lower than the temperatures at which they appreciably react are problematic to characterize using traditional ultrahigh vacuum surface science methods.\(^9\) To measure extremely low dissociative sticking coefficients, such as those for methane on Ni surfaces, intermediate pressure “thermal bulb” techniques were developed by Yates and Goodman,\(^10\) and later extended by Chorkendorff.\(^11\) Heating a surface in an ambient gas at a pressure of several Torr\(^6\) can permit collisional energy transfer to thermalize the gas layer within a mean free path of the surface to the surface temperature such that a thermal dissociative sticking coefficient can be measured. For a single pure gas, the pressures required for thermalization coupled with a gas–surface collision flux of \(~10^9\) monolayers s\(^{-1}\) Torr\(^{-1}\) tends to make the thermal bulb technique best suited for measurements of thermal dissociative sticking coefficients less than \( S(T) \sim 10^{-6} \) because otherwise the dosing times become overly short. However, if the reactive gas is diluted in an inert buffer gas, higher values of \( S(T) \) can be measured\(^1\) while maintaining the several Torr net pressure typically required for local gas/surface thermalization.\(^9\) Super-
sonic molecular beams provide an important means to investi-
gate nonequilibrium dissociative sticking coefficients as a
function of a molecule’s translational energy and internal energy,
and the surface temperature. 3,12–15 With the aid of laser-pumped
supersonic molecular beams, rovibrational eigenstate-resolved
dissociative sticking coefficients for methane16–18 and silane19
have begun to be measured. The reactivity of methane on a
variety of metal surfaces has not been found to be purely
statistical. Rovibrational efficiencies for reaction relative to normal
translational energy have been determined to vary over the range
0.4 ≤ ηv ≤ 1.4, with an average to date of ⟨ηv⟩ = 0.88.20 The
value of ηv appropriate to statistical transition state theories of
chemical reactivity is ηv = 1.

Molecules in supersonic molecular beams have undergone
collisionally induced rotational and vibrational cooling during
their supersonic expansion that can leave each molecular
vibrational mode at a different temperature.21 For small mol-
ecules, such as methane, vibrational cooling is inefficient and
the vibrational modes stay close to the nozzle temperature of
the molecular beam, although the rotational temperature falls
considerably.22 Larger alkanes are anticipated to undergo more
substantial vibrational and rotational cooling during supersonic
expansions, which make them, in the absence of detailed hot
band spectroscopic characterization that could determine their
state distributions and energy content, somewhat ambiguous
subjects for readily interpretable kinetic studies of gas–surface
reactivity. Nevertheless, Madix’s pioneering supersonic molec-
ular beam studies23 of light alkane dissociative chemisorption
on Pt(111) established that the alkane dissociative sticking
coefficients scale with the normal translational energy of the
impinging molecules, $E_n = E_e \cos^2(\vartheta)$, where $E_e$ is the
molecular translational energy and $\vartheta$ is the angle of incidence measured
away from the surface normal. In the current study, a heated
effusive molecular beam was used to prepare alkanes with
thermal energy distributions and to send the molecules toward
a Pt(111) surface along the direction of the surface normal.
Dissociative sticking experiments were performed in an ultrahigh
vacuum surface analysis machine that maintained pressures less
than $5 \times 10^{-5}$ Torr during effusive beam dosing such that
$S_0(T_s T_g)$ values over the sometimes problematic range from $10^{-2}$
to $10^{-6}$ could be conveniently measured. The subscript $n$ on $S_0$
denotes sticking for a beam aimed normal to the surface. For
these alkanes whose sticking scales with normal translational
energy, effusive beam experiments with $T_g = T_s = T$ determined
$S_0(T)$, a close approximation and formal upper bound to the
thermal dissociative sticking coefficient, $S(T)$ [vide infra; compare
$S(T)$ and $S_0(T)$ simulations in Figures 2–5 and note
Table 2 where $S(T = 700 \text{ K})/S_0(T = 700 \text{ K}) = 0.74$]. In this
way, the effusive beam technique allows for the investigation
of quasi-thermal reactivity that is relevant to high pressure
catalysis at comparable temperatures. Under thermal equilibrium
conditions, detailed balance requires that the net gas–surface
energy transfer sums to zero, but this is not the case when $T_g \neq T_s$. Consequently, measurements of nonequilibrium $S_0(T_s, T_g)$
provide opportunities to characterize gas–surface energy transfer
under conditions where energy transfer and reactivity are
intimately coupled. A microcanonical unimolecular rate theory
model24–26 of dissociative chemisorption sufficed to analyze the
alkane $S_0(T_s, T_g)$ data and extract transition state and gas–surface
energy transfer parameters.

II. Experimental Section

The basic experimental methodology for measuring alkane
dissociative sticking coefficients with effusive molecular beams
has been previously described27,28 and only a brief synopsis of
the current apparatus and procedures follows. The experiments
were performed in an ultrahigh vacuum (UHV) surface analysis
chamber with a base pressure of $1 \times 10^{-10}$ Torr. The chamber
was pumped by a 240 L/s ion pump, 210 L/s turbomolecular
pump, and a cryogenically cooled Ti sublimation pump (TSP).
The chamber is equipped with a double-pass cylindrical mirror
analyzer for Auger electron spectroscopy (AES), a residual gas
analyzer, a twice-differentially pumped quadrupole mass spect-
rometer for thermal programmed desorption, a thin-walled
aperture calibrated leak from Vacuum Technology Inc., and a
variable temperature, effusive molecular beam doser. Gas
pressures in the chamber were measured using a Stabil-Ion
Bayard-Alpert gauge from Granville-Phillips as well as an MKS
model 615 bakeable Baratron gauge with a model 670 signal
conditioner. When alkanes were dosed into the chamber, the
ion pump and TSP were separated from the main chamber by a
gate valve, to maintain a constant chamber pumping speed
based on the turbopump alone. A Pt single crystal of 10 mm
diameter × 1.5 mm thickness with a surface oriented to within
0.1° of the (111) face was obtained from Surface Preparation
Laboratory, Zaandam, The Netherlands, and used in these
experiments. The Pt(111) surface was cleaned by cycles of Ar+ ion
sputtering at 800 K, followed by annealing at 1200 K for 5 min.
To remove C contaminants, the sample was oxidized at 800 K under $5 \times 10^{-9}$ Torr of O2. The sample’s initial cleanliness and C accumulation after alkane dosing was
monitored by AES. Gases used for dosing and C calibration
were research grade methane (99.999%), ethane (99.995%), and
propane (99.993%), and CP grade ethylene (99.5%), which were
purchased from Matheson Tri-Gas and used without further
purification.

An effusive molecular beam doser that could be heated to
1200 K was used to dose molecules onto the Pt(111) surface
along the direction of the surface normal. The doser was a 0.25 in.
diameter 304 stainless steel tube terminating in a 0.010 in.
thickness wall with a 0.197 in. (0.50 mm) diameter exit hole.
The last 4 in. of the stainless steel tube was covered by a close
fitting alumina sleeve that was wound with 0.010 in. diameter
W wire that was used to resistively heat the doser nozzle. These
last 4 in. of the doser were coated with Aremco no. 569 alumina
paste to sufficient depth that the W wires were buried to increase
the thermal efficiency of the nozzle heating and to eliminate
interaction of the dosing molecules with the hottest portions of
the W heating wire. A K-type thermocouple spot-welded to the
stainless steel exit wall of the nozzle served to monitor the
nozzle temperature, which was assumed to coincide with the
gas temperature, $T_g$, of the exiting, effusing molecules.
Evidence that the effusive molecules reach the nozzle temper-
ature stems from residual gas analysis that showed the onset
for thermal cracking of propane from the heated nozzle occurs
at $T_g = 960 \text{ K}$, which is in good accord with a recent pyrolysis
study.29 Cracking of the lighter alkanes occurs at sufficiently
higher temperature that it could not be conveniently observed.
In operation, the effusive doser was positioned 10 mm away
and directly facing the center of the Pt(111) sample. There are
two fluxes that strike the sample surface when the effusive doser
is used: (i) the direct flux of gas at $T_g$ from the molecular beam,
and (ii) the background flux of gas assumed to have become
thermalized to the 300 K chamber wall temperature that initially
derived from the heated doser but which has not yet been
chemisorbed or pumped away. The ratio of these fluxes for CH4
is roughly 6:1 for this dosing configuration. Chamber pressures
during dosing were typically held in the range from $5 \times 10^{-5}$
to $3 \times 10^{-8}$ Torr to avoid any instability in ion gauge pressure measurements due to electron stimulated desorption.\textsuperscript{30} The chamber ion gauge was turned off during alkane dissociative sticking experiments to avoid any possibility that stray electrons might crack some alkanes. A calibration curve was used to calculate the chamber pressure based on the pressure read by a Baratron on the gas manifold feeding the effusive doser. The chamber pumping speed for the dosed gas of interest was measured using the thin-walled aperture calibrated leak (calibrated over 3 orders of magnitude for $N_2$). The absolute flux through the effusive source was also determined using the calibrated leak. Ion gauge sensitivity factors for the different gases were experimentally determined by comparing ion gauge readings to those of the chamber's bakeable Baratron. Gas sensitivity factors (relative to $N_2$) were found to be 1.6, 2.6, and 3.7 for methane, ethane, and propane, respectively, in close accord with literature values.\textsuperscript{31}

In the effusive molecular beam experiments, dissociatively chemisorbing alkane molecules are assumed to yield alkyl radicals whose $C$ remains on the surface, independent of any secondary chemistry. The initial dissociative sticking coefficient, $S_0(T_g,T_s)$, was determined from effusive beam experiments by measuring the carbon coverage, $\theta_c$, deposited on the surface after dosing for a time $\tau$ with a known beam flux based on knowledge of the chamber pressure, $p_c$, and pumping speed, $C_c$. The heated gas that misses or does not react with the Pt(111) surface was made by AES. Spectra were obtained over the thin aperture wall.

Carbon coverages were determined by fitting the undifferentiated AES spectra using the CasaXPS program and comparing the relative intensities of the Pt$_{237}$ and C$_{272}$ peaks. The AES peaks are labeled traditionally according to their elemental source and energetic position in electronvolts within differentiated AES spectra. A Shirley background subtraction over the interval from 210 to 280 eV was applied to the undifferentiated AES spectra and was found to give more consistent analytical results than either a linear or Tougaard subtraction. Peak fitting was initially optimized for a clean Pt(111) AES spectrum. A convolution of 30% Lorentzian and 70% Gaussian was used to fit the Ar$_{219}$, Pt$_{237}$, and the C$_{272}$ peaks using the Marquardt nonlinear least-squares fitting routine. Peak positions were constrained to 221 eV (Ar$_{219}$), 233 eV (Pt$_{237}$), and 248 eV (Pt$_{248}$), but the C$_{272}$ peak position was not constrained. FWHM constraints were applied to Ar$_{219}$ (11.7 eV), Pt$_{237}$ (12.5 eV), Pt$_{248}$ (11.2 eV), and C$_{272}$ (15 eV) peaks. Peak area ratios were also constrained and set for Pt$_{238}/$Pt$_{237}$ to 0.48 and for Ar$_{219}/$Pt$_{237}$ to 0.15. The carbon coverage was given by the scaled peak area ratio $\theta_c = 0.61$ C$_{272}$/Pt$_{237}$ for AES excitation using a 3 keV electron beam. This relationship was verified by dosing ethylene to give standard C coverages. A saturated monolayer of ethylene formed at $T_s = 300$ K gave a C coverage of 0.46 ML\textsuperscript{33} whereas extended dosing of ethylene at $T_s = 1000$ K gave a saturated monolayer of graphene with a C coverage of 2.57 ML.\textsuperscript{34} The alkane deposition and C calibration experiments were performed at $T_s \leq 1000$ K, which ensured there was negligible C diffusion into the bulk of the Pt(111) sample.

The reported dissociative sticking coefficients have a typical statistical error of $\pm 20\%$. With the aid of the calibrated leak, we discovered that earlier effusive beam experiments for methane\textsuperscript{27} and ethane\textsuperscript{28} on Pt(111) suffered from two problems: (i) an assumed ion gauge constant that was in error and (ii) an insufficiently accurate conductance calculation relating the pressure at the nozzle manifold to the pressure at the nozzle orifice (we now directly measure an equivalent working curve). The average net effect was that the earlier effusive beam work reported sticking coefficients that were roughly 3-fold too low.

### III. Theoretical

A microcanonical unimolecular rate theory (MURT) model of activated dissociative chemisorption has been described elsewhere\textsuperscript{24–26} and its application to alkanes, RH, is schematically summarized in Figure 1. The kinetics can be described as following a precursor-mediated microcanonical trapping mechanism in which gas−surface collision complexes composed of an incoming molecule and a few local surface oscillators have their pooled energy microcanonically randomized such that the molecules become trapped in the physiosorption well located between the transition states for reaction (dissociative chemisorption) and desorption. These physisorbed complexes (PCs) go on to react or desorb with RRKM rate constants,
where \( W_i(E - E_i) \) is the sum of states for transition state \( i = D, R \) with threshold energy for reaction \( E_i \) (e.g., \( E_R = E_0 + E_0 \) in Figure 1), \( p(E) \) is the PC density of states, and \( h \) is Planck’s constant. On the offentimes convenient \( E^* = E - E_0 \) energy scale, whose zero occurs for the reactants at infinite separation, the apparent threshold energy for reaction is \( E_0 \). Lifetimes for molecular desorption at reactive energies \( (E^* \geq E_0) \) are ultrafast for small molecules that have a relatively shallow physisorption well and a high threshold energy for dissociative chemisorption. In such cases, ignoring energy exchange between the PCs and the surrounding metal bulk can be a good approximation. For example, methane on Pt(111) with \( E_0 = 16 \) kJ/mol and \( E_0 = 50 \) kJ/mol has a calculated RRKM desorption lifetime of \( \tau_\text{cal} = 3 \times 10^{-12} \) ps (vide infra). Ignoring energy transfer between the PCs and their surroundings yields the PC-MURT model of dissociative chemisorption that has been successfully applied to \( \text{H}_2/\text{Cu}(111) \) dissociative chemisorption/associative desorption dynamics,39 CO\(_2/\text{Rh}(111) \) dissociative chemisorption/CO oxidation dynamics,36 \( \text{CH}_4 \) dissociative chemisorption on Pt(111),27 Ni(100),37,38 Ir(111),39 and Ru(0001),7 and Si\(_2\)H\(_4 \) dissociative chemisorption on Si(100).40 RRKM desorption lifetimes at reactive energies for larger alkanes increase due to the increasing depth of the physisorption well, increasing number of vibrational modes, and the falling threshold energy for dissociative chemisorption [e.g., \( \tau_{\text{cal}}(E^*=E_0) = 44 \) ps for propane/Pt(111)]. Consequently, the more general Master-Equation (ME)-MURT model that explicitly treats vibrational energy exchange between the PCs and the surrounding metal was required to adequately treat the reactivity of the higher alkanes. The ME for the PC coverage distribution is

\[
\frac{d\theta_p(E)}{dt} = F_0 f(E) \left( k_R(E) + k_D(E) \right) \theta_p(E) + \int_0^{E'} \left( R(E,E') \theta_p(E') - R(E',E) \theta_p(E) \right) dE' \tag{4}
\]

where \( F_0 \) is the incoming molecular flux in ML/s, \( f(E) \) is the flux distribution for forming a PC at energy \( E \), \( k_R(E) \)'s are RRKM rate constants, and \( R(E,E') \) is the rate distribution for PC/metal energy transfer that takes PCs at energy \( E' \) to energy \( E \). In analogy to collisional energy transfer in the gas phase,41 \( R(E,E') \) is factored as \( \omega P(E,E') \), the product of a collision frequency, \( \omega \), times a collision step size distribution, \( P(E,E') \). For PC/metal energy transfer, \( \omega \) was taken to be 3 times the mean phonon frequency of the bulk metal because the PCs are bathed by phonons incoherently from three directions. The alkane ME-MURT calculations employed a simple exponential down model of the PC/phonon collision step size distribution, described for downward energy transfer as

\[
P(E,E') = \frac{1}{N(E')} \exp\left( -\frac{E' - E}{\alpha} \right) \quad \text{where} \quad E' - E > 0
\tag{5}
\]

where \( N(E') \) is a normalization constant and \( \alpha \) is equal to \( 1/(\Delta E_\text{down}) \), the mean energy transferred in a downward “PC/phonon collision”. The upward energy transfer is fixed by the detailed balance requirement that the net energy transfer should be zero under thermal equilibrium conditions. The detailed balance requirement is simply that the bracketed term within the integral of eq 4 must be zero for a thermal physisorbed complex distribution. Experimental dissociative sticking coefficients were simulated using

\[
S = \frac{1}{F_0} \frac{d\theta_p}{dt} = \frac{1}{F_0} \int_0^{E'} k_R(E) \theta_p(E) dE \tag{6}
\]

where the steady state physisorbed coverage distribution, \( \theta_p(E) \), was found by solving the eq 4 ME using standard energy graining and matrix methods.42,43

Weaver and Madix23 showed that the dissociative sticking coefficients for light alkanes on Pt(111) obey normal translational energy scaling and so translational energy parallel to the surface was taken to be a spectator degree of freedom. Energy associated with all other molecular degrees of freedom and the energy of 5 surface oscillators was assumed to be active exchangeable energy within the PCs formed. Dissociative sticking calculations require specification of the transition states for desorption and reaction, as well as the energy transfer parameter, \( \alpha \). The desorption transition state was taken to occur when the alkane was freely rotating and vibrating in the gas phase, far from the surface oscillators of the united PC. The surface oscillators were assumed to vibrate at the mean phonon frequency of the metal \( \nu_s = \sqrt{3} \sqrt{\omega_0 T_{\text{bath}}/h} \), yielding 122 cm\(^{-1}\) for Pt. The desorption coordinate was taken as the vibrational, ultimately translational, motion along the surface normal and
A. Methane. Dissociative sticking coefficients for methane on Pt(111) are presented as Arrhenius plots over the T̃ range from 400 to 1000 K in Figure 2. The background sticking for ambient gas at the 300 K chamber temperature, S_bg(T̃,T̃_e) = S(T̃ = 300 K,T̃_e), was determined from experiments in which methane was dosed through the calibrated leak whose orifice had no line-of-sight to the Pt(111) surface. Effusive molecular beam experiments directed along the Pt(111) surface normal were performed for T̃_g = 900, 800, 700, 600, and 300 K at some T̃_e to yield S_g(T̃_g,T̃_e) and S_e(T̃_e) values according to eq 1. The lines near the experimental data points are PC-MURT simulations based on a transition state parameter set {E_0 = 56 kJ/mol, s = 3, v_0 = 125 cm^-1},^27 that reproduces a wide variety of methane/Pt(111) supersonic molecular beam experiments.^56,49

Measurement of S_bg(T̃_g = 300 K,T̃_e = 400 K) = 1.3 × 10^-7 required dosing 4 × 10^-4 Torr of ambient CH₄ gas for ~3 h. The theoretical curve for S_bg(T̃_g = 300 K,T̃_e ≤ 500 K) is suggestive that the background sticking coefficients reported at the lowest T_e values may be influenced by an approach to a limiting low sticking value attainable with our current experimental procedures. Impurities in the methane gas dosed were not discerned by residual gas analysis, but it may be that additional purification of the gas would permit lower sticking coefficients to be measured. A tunneling contribution^57 to the dissociative sticking coefficient could also tend to flatten the Arrhenius plot at low T_e. At the higher gas temperatures, S_g(T̃_g ≥ 600 K,T̃_e ≤ 500 K) values calculated using eq 1 would be negligibly impacted if the reported S_bg(T̃_g = 300 K,T̃_e ≤ 500 K) values were overestimates because in the effusive beam experiments the directed molecular flux hitting the surface was ~6 times higher than the indirect flux and the sticking coefficient of the directed hot gas was already more than 100 times higher than the reported S_bg(T̃_g = 300 K,T̃_e ≤ 500 K) values for the ambient gas, so the background sticking correction in eq 1 was already negligible.

The roughly 2.5-fold discrepancy between the PC-MURT simulations and the effusive beam experiments may derive from several causes. As a transition state theory, the PC-MURT is likely to parametrize a reactive transition state as looser when experimental reactant energies are hyperthermal and a broader range of phase space above the transition state can be energetically accessed as compared to the case for a more energy starved thermal reaction. This may explain some, or perhaps all, of the discrepancy. On the other hand, Beck and co-workers^48 have shown that the vibrational efficacy for dissociative chemisorption of CH₄ on Pt(111) for 2 quanta of C–H asymmetric stretch is only η_ν(2ν_3) = 0.38, suggestive of an early transition state according to the Polanyi rules^49 for direct reactions. If vibrational energy is generally less efficacious in promoting reaction than E_ν for CH₄/Pt(111), then the statistical PC-MURT, which assumes η_ν = 1, may fail to quantitatively predict variations in dissociative sticking coefficients across disparate kinds of experiments. Other dynamical biasing effects are possible (e.g., a minimum E_v requirement to access the transition state barrier region of the potential energy surface) that could lead to deviations from the statistical PC-MURT predictions. Finally,
there may still be some subtle unrecognized systematic errors in the two sets of nonequilibrium experiments being compared that might limit theoretical modeling. An example would be if the molecules behind the beam nozzles did not come into full thermal equilibrium with the nozzle wall temperatures before their exit through the nozzle apertures. Overall, using the intermediary of the PC-MURT model, agreement between the supersonic molecular beam experiments and the effusive molecular beam experiments is reasonably good.

**B. Ethane.** Figure 4 compares dissociative sticking coefficients for ethane on Pt(111) with PC-MURT and ME-MURT simulations using a parameter set optimized for the ME-MURT. Ethane reacts more readily with the surface than methane, and the effects of gas–surface energy transfer are more apparent. With the optimized energy transfer parameter of $R_g = 1400$ cm$^{-1}$, the ME-MURT simulations of $S_n(T_g,T_s)$ dramatically collapse the PC-MURT (equivalent to the ME-MURT with $\alpha = 0$) simulations toward the thermal dissociative sticking coefficient, $S(T)$, prediction. Overall, the ME-MURT simulations reproduce the propane $S_n(T_g,T_s)$ data reasonably well.

**C. Propane.** Figure 5 compares dissociative sticking coefficients for propane on Pt(111) with PC-MURT and ME-MURT simulations using a parameter set optimized for the ME-MURT. Propane reacts more readily with the surface than ethane, and the effects of gas–surface energy transfer are more apparent. With the optimized energy transfer parameter of $\alpha = 1400$ cm$^{-1}$, the ME-MURT simulations of $S_n(T_g,T_s)$ dramatically collapse the PC-MURT (equivalent to the ME-MURT with $\alpha = 0$) simulations toward the thermal dissociative sticking coefficient, $S(T)$, prediction. Overall, the ME-MURT simulations reproduce the propane $S_n(T_g,T_s)$ data reasonably well.
TABLE 1: MURT Dissociative Sticking, Energy Transfer, and Desorption Parameters for Alkanes on Pt(111)

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<tr>
<td></td>
<td>$E_0$ (kJ/mol)</td>
<td>$s$</td>
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<td>50.2</td>
<td>3</td>
</tr>
<tr>
<td>ethane</td>
<td>33.8</td>
<td>4</td>
</tr>
<tr>
<td>propane</td>
<td>20.7</td>
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Figure 5. Propane dissociative sticking coefficients on Pt(111) are compared with (a) PC-MURT simulations based on the parameter set {$E_0 = 20.7$ kJ/mol, $s = 4$, $\nu_D = 65$ cm$^{-1}$} and (b) ME-MURT simulations that additionally incorporate gas–surface energy transfer with exponential down parameter $\alpha = 1400$ cm$^{-1}$. The $S_s(T)$ points from direct effusive beam experiments for which $T_s = T_d = T$ are additionally labeled by encirclement.

TABLE 2: Arrhenius Fit Parameters to Experimental $S_s(T)$ and Theoretical ME-MURT $S(T)$ for Alkanes on Pt(111)

<table>
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<th>$S_s(T)$ = $S_0$ exp$(-E_s/RT)$</th>
<th>$S(T)$ = $S_0$ exp$(-E_s/RT)$</th>
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</table>

Figure 6. Arrhenius plot of quasi-thermal dissociative sticking coefficients, $S_s(T)$, for several alkanes on Pt(111) with one standard deviation error bar included. The effusive molecular beam was incident along the direction of the surface normal with $T_s = T_d = T$. Table 2 lists the parameters of the fitted Arrhenius lines.

D. Quasi-Thermal Dissociative Sticking, $S_s(T)$. Quasi-thermal dissociative sticking coefficients, $S_s(T)$, measured with normally incident effusive molecular beams are shown in Figure 6 for the light alkanes on Pt(111). Table 2 compares the Arrhenius fit parameters for the $S_s(T)$ data with Arrhenius fit parameters for the ME-MURT calculated thermal dissociative sticking coefficients, $S(T)$, of Figures 3–5 evaluated near $T = 700$ K. The Arrhenius fit to the propane $S_s(T)$ experiments excluded the somewhat statistically irregular point at $T = 400$ K under the suspicion that the chamber residual gases, H$_2$ and CO, could build up low but measurable coverages on Pt(111) at surface temperatures less than 500 K, which might influence the alkane sticking in subtle ways.

The MURT simulations of Figure 3–5 show that the quasi-thermal dissociative sticking coefficient $S_s(T)$ should provide an upper bound, but still close approximation, to the thermal dissociative sticking coefficient $S(T)$. This should be generic behavior for the light alkanes whose dissociative sticking coefficients scale with $E_n$. This is because more $E_n$ ($= E_i \cos^2(\theta)$) is available to enhance reaction when the thermal molecular flux is directed normally at $\theta = 0^\circ$ as compared to when the flux derives from a random thermal ambient gas impinging with a $\cos(\theta)/\tau$ angular distribution. For example, the mean $E_n$ of a normally directed thermal effusive beam is $\langle E_n \rangle = 2k_BT$, whereas integrated over a thermal ambient flux $\langle E_n \rangle = k_BT$. The difference between $S_s(T)$ and $S(T)$ stems only from the difference in the $E_n$ energy distributions for effusive beam and ambient gas impingement. As the alkane complexity
with increasing alkane complexity will further serve to drive complexity increases. Increasing gas temperature limits of the MURT dissociative sticking coefficients the assumption that the alkane

Both the thermal effusive beam and TPD experiments indicate TPD experiments for which the octane desorption peak Figure 7 extrapolated value of n

E_a [kJ/mol]

E_a = γ E_D + E_a,0

γ = 0.94

E_D = 72.9 kJ/mol

Methane

Ethane

Propane

Hexane

Heptane

Octane

Desorption Energy, E_D [kJ/mol]

Figure 7. Evans—Polanyi plot of the S_n(T)-derived activation energy for dissociative chemisorption versus desorption energy for several alkanes on Pt(111) [solid points measured; open points extrapolated].

increases, and more degrees of freedom contribute to the actively exchangeable energy E within the PCs, the fractional contribution of E_a to E will diminish. Consequently, the relative difference between S_n(T) and S(T) should diminish as the alkane complexity increases. Increasing gas—surface energy transfer with increasing alkane complexity will further serve to drive S_n(T) toward S(T).

The S_n(T) and S(T) parameters of Table 2 are comparable and on average S(T = 700 K)/S_n(T = 700 K) = 0.74. The high temperature limit of the MURT dissociative sticking coefficients is S → 1, though an Arrhenius parametrization holds well at lower temperatures where S ≤ 10^{-5}. Consequently, there is no “physical problem” with any S_n value in Table 2 exceeding 1—there is simply only a finite range of T over which an Arrhenius form is appropriate for fitting a dissociative sticking coefficient. Without imposing any theoretical model, the experimentally easier to determine S_n(T) is likely able to serve as a sufficiently accurate approximation to S(T) for most purposes.

E. Evans—Polanyi Relation. Figure 7 is a plot of the experimental S_n(T)-derived thermal activation energy, E_a, for dissociative chemisorption versus the desorption energy, E_D, of the light alkanes on Pt(111). The plot is linear with a slope of −0.94. Figure 7 also provides some extrapolated estimates of E_a for larger n-alkanes with known desorption energies. Tait et al. measured desorption energies for a series of n-alkanes on Pt(111) and found that octane was the smallest n-alkane for which some dissociative chemisorption was detectable in thermal programmed desorption (TPD) experiments. The Figure 7 extrapolated value of E_a = 5.2 kJ/mol for dissociative chemisorption of octane seems in reasonable accord with the TPD experiments for which the octane desorption peak occurred at 277 K (cf., E_a with RT = 2.3 kJ/mol at 277 K). Both the thermal effusive beam and TPD experiments indicate that the activation energy for dissociative chemisorption of n-alkanes falls as the alkane size and desorption energy increases.

Figure 7 can be interpreted as an Evans—Polanyi plot under the assumption that the alkane E_D serves as a good approximation to the van der Waals stabilization energy of the chemisorbed alkyl radical product of dissociative chemisorption. Via a Haber cycle, the reaction exergonicity, ΔE, for dissociative chemisorption of an n-alkane RH can be broken down as the energy required to break an R—H bond in the gas phase minus the sum of a C—Pt(111) covalent bond energy, a H—Pt(111) covalent bond energy, and the van der Waals stabilization energies for the chemisorbed R and H radicals on Pt(111).

Assuming the van der Waals stabilization energy of chemisorbed R is well approximated by E_D for RH, and the variation of the R—H bond energy is negligible in comparison to the variation of E_D with alkane size, then a reasonable approximation should be ΔE = ΔE_s = γ E_D + (γ ε + β) where 0 ≤ γ ≤ 1 and β is a constant. A value of γ near 0 is indicative of an early transition state that resembles the reactants such that E_a varies little in response to variation in the product state energy, and consequently to variation in ΔE. Conversely, a value of γ near 1 is indicative of a late transition state that resembles the products such that E_a varies in close accord to variation in the product state energy and ΔE. Substituting our approximate ΔE for the n-alkanes on Pt(111), yields E_a = γ E_D + (γ ε + β) where the bracketed term is a constant. The slope of the Figure 7 E_a versus E_D plot yields γ = 0.94, a value indicative of a late transition state.

F. Comparison to Other Work. The Evans—Polanyi relation embodied in Figure 7 is an important one because it suggests that the many electron van der Waals interaction between the chemisorbed products of dissociative chemisorption and the surface plays a dominating role in determining the variation of the activation energy for dissociative chemisorption of the n-alkanes. Typical generalized gradient approximation density functional theory (DFT) calculations of reaction energetics do not directly account for van der Waals interactions. In consequence, DFT calculated threshold energies for alkane dissociative chemisorption on metals typically vary little with alkane size. Adding van der Waals corrections to DFT calculated reaction energetics is only beginning to be explored in the theoretical literature of alkane reactivity at surfaces. It is interesting to consider that the sum of pairwise van der Waals interactions between a molecule and the atoms of a solid will depend on the shape of the intervening surface, flat or curved, and the electronic properties of the solid’s atoms. Consequently, the van der Waals stabilization energy of alkanes at a surface may show enough variation between the case of a flat surface of a bulk solid and the curved surface of a small nanoparticle that size dependent reactivity changes may result. This might afford opportunities for tuning alkane reactivity through control over nanocatalyst size and shape.

Electronic structure theory (EST) calculations of the threshold energy for dissociative chemisorption of CH_4 on Pt(111) have produced a range of E_0 values: 43 kJ/mol, 57 kJ/mol, 61 kJ/mol, 71 kJ/mol, 74 kJ/mol. MURT analysis of our CH_4/Pt(111) effusive beam experiments gave transition state parameters \{E_0 = 50.2 kJ/mol, s = 3, ν_D = 205 cm^{-1}\}, whereas a similar MURT parameter set of \{E_0 = 56 kJ/mol, s = 3, ν_D = 125 cm^{-1}\} optimized simulations of dissociative sticking coefficients for nonequilibrium, hyperthermal, supersonic molecular beam experiments. A reasonable experimentally based estimate of E_0 is therefore E_0 = 53 ± 3 kJ/mol, which is toward the lower end of the range of E_0 calculated by EST. If one’s interest is to employ the gas—surface reactivity measured under controlled surface science conditions to predict thermal rate constants of the kind appropriate to high pressure catalysis, then the transition state parameter set derived from the effusive molecular beam experiments is likely preferable. The gas—surface collisions in the effusive beam experiments should better mimic the collisions occurring under thermal equilibrium conditions, particularly for S_n(T) measurements, than the collisions occurring in hyperthermal, supersonic molecular beam experiments. Furthermore, transition state theory is optimally applied to
thermal systems where the majority of reactive trajectories are constrained to pass very close in energy to the transition state along the minimum energy pathway linking reactants to products because of the thermal Boltzmann weighting of high energy states. Transition state theory applied to higher energy, non-equilibrium situations may be complicated by needs to incorporate gas–surface energy transfer and anharmonic corrections to the description of the transition state and to account for additional reactive pathways that may begin to open up at higher energies. Consequently, it seems that characterization of the CH4/Pt(111) transition state parameters based on the effusive beam experiments is preferable and so E0 = 50 kJ/mol is our experimentally based estimate of the threshold energy for dissociative sticking of CH4 on Pt(111).

Alkane dissociative chemisorption is structure sensitive and Sbkg(Tg) values for CH4 and C2H6 ambient gases\(^2\) impinging on Pt(110) are higher than those reported here for Pt(111). Sun and Weinberg\(^6\) extracted Eb = 60 kJ/mol for CH4 and E0 = 12 kJ/mol for C2H6 from their Sbkg(Tg = 300 K, Td) measurements on Pt(110). Note that such nonequilibrium dissociative sticking coefficients Sbkg(Tg = 300 K, Td) are not equivalent to the thermal dissociative sticking coefficient, ST, nor Sd(T), as is apparent from Figures 2–5. Wei and Iglesia\(^5\) have shown that methane reforming over supported Pt nanocatalysts is structure sensitive and rate limited by methane dissociative chemisorption at temperatures near 873 K and 1 bar pressure. The apparent thermal dissociative sticking coefficient derived from Iglesia’s turnover rate constants for 2 nm Pt nanocatalysts is S(T) = S0 exp(−Ea/RT)\(^2\) where S0 = 3.1 × 10^{-2} and Ea = 80 kJ/mol, which leads to S(T = 700 K) = 3.3 × 10^{-8}. The apparent S(T) for CH4 on these Pt nanocatalysts at 700 K is ~6000-fold less than that expected for Pt(111) according to Table 2. Such a discrepancy might result if most surface sites on the working nanocatalysts were poisoned by C buildup such that apparent turnover rates based on the net number of Pt surface sites were artificially low, or if CH4 dissociative chemisorption is not the only kinetic limitation imposed in methane reforming. The CH4/Pt nanocatalyst activation energy of Ea = 80 kJ/mol is higher than the activation energies of E0 = 56 kJ/mol [S(T)] and 58 kJ/mol [Sd(T)] determined here for CH4/Pt(111), and also the Ea = 60 kJ/mol [Sbkg(Tg = 300 K, Td)] value measured for CH4/Pt(110).\(^6\)

DFT calculations for C2H6 dissociative chemisorption on Pt surfaces find E0 = 52 kJ/mol for Pt(111),\(^5\) and two transition states for Pt(110) with E0 = 37 kJ and 41 kJ/mol.\(^5\) MURT analysis of our C2H6/Pt(111) effusive beam experiments gave E0 = 34 kJ/mol. A thermal bulb study of C2H6/Pt(111) dissociative sticking\(^5\) over the temperature range from 515 to 635 K measured a S(T) that at T = 600 K was roughly 130-fold smaller than the S0(T) measured here. The activation energy for the thermal bulb S(T) was E0 = 37 ± 3 kJ/mol. Our C2H6/Pt(111) effusive beam experiments led to activation energies of E0 = 44.3 kJ/mol [S(T)] and 42.7 kJ/mol [Sd(T)], as reported in Table 2.

A recent DFT study examined C2H6 dissociative chemisorption on Pt4 subnanometer catalysts and on Pt(111).\(^6\) Threshold energies for dissociative chemisorption of E0 = 17 kJ for the Pt4 clusters and E0 = 114 kJ/mol for a Pt(111) surface were calculated. It was claimed that the lower threshold energy for Pt4 would make subnanometer Pt catalysts more active for oxidative dehydrogenation of propane than nanometer Pt catalysts whose surfaces might more closely resemble Pt(111). MURT analysis of our effusive beam experiments for C2H6 dissociative sticking on Pt(111) found E0 = 21 kJ/mol, far smaller than the DFT prediction for Pt(111) but fairly close to the DFT prediction for Pt clusters.

**G. Gas–Surface Energy Exchange.** The nonequilibrium dissociative sticking coefficients Sd(T, Td) for ethane and propane on Pt(111) provide clear evidence for substantive gas–surface energy transfer. As discussed above, the net gas–surface energy transfer must sum to zero under thermal equilibrium conditions by detailed balance, and so the thermal dissociative sticking coefficient S(T) is not influenced by specific rates of gas–surface energy transfer\(^6\) [cf., PC-MURT (α = 0) and ME-MURT (α = 1400 cm\(^{-1}\)) simulations of the propane S(T) in Figure 5]. As a close approximation to S(T), the quasi-thermal dissociative sticking coefficients Sd(T, Td) measured in effusive beam experiments is relatively insensitive to changes in gas–surface energy transfer rates, particularly for larger molecules with many degrees of freedom. Ultimately, the experimental hallmark of gas–surface energy transfer is the tendency of the nonequilibrium dissociative sticking coefficients Sd(T, Td) to collapse toward the S(T) curve (or its Sd(T) surrogate).

The gas–surface energy transfer parameters of α = 50, 350, and 1400 cm\(^{-1}\) for methane, ethane, and propane on Pt(111) are believed to be among the first to be determined at reactive energies for molecules interacting with a clean metal surface for the eq 5 kind of exponential energy down energy transfer model that is commonly employed in studies of gas phase energy transfer and reactivity.\(^41–43\)

Finally, it is worth reconsidering the Figure 7 Evans–Polanyi plot based on the premise that E0 = γΔE + β ≈ −γE0 + E0,0. The slope of Figure 7 yields γ = 0.94, which is indicative of a late transition state for dissociative chemisorption. Although DFT calculations overestimate the experimentally determined threshold energies for alkane dissociative chemisorption on Pt(111), DFT studies typically find late transition states for dissociative chemisorption such that γ ~ 0.9 for ΔE changes.\(^25\)

With regards to there is good agreement between DFT and our experiments that provides bolstered assurance that the transition state for alkane dissociative chemisorption is later on Pt(111). Interestingly, Beck and co-workers\(^45\) have experimentally shown that the vibrational efficacy for dissociative chemisorption of CH4 on Pt(111) for 2 quanta of C–H asymmetric stretch is ηv(2ν) = 0.38, suggestive of an early transition state according to the Polanyi rules\(^6\) for direct reactions. A vibrational efficacy of ηv(2ν) ≥ 1 for promoting reaction with respect to E0 would be anticipated for a late transition state.\(^20\) It is hard to reconcile the dynamical result with DFT’s and the effusive molecular beam experiments’ prediction of a late transition state. However, state-selective reactivity in polyatomic molecules, even in the gas phase,\(^6\) is not as well understood as the atom + diatomic molecule reactivity for which the Polanyi rules were developed. Unfortunately, there are no additional eigenstate-resolved measurements of ηv for other vibrational modes available that might establish an average (ηv) closer to or greater than 1 for the CH4/Pt(111) reactive system. Within the context of considering dynamical excursions away from a precursor mediated microcanonical trapping (MURT) reaction mechanism, ηv values may depend primarily on E0 and vibrational state dependent variations in the intramolecular vibrational energy redistribution (IVR) and gas–surface energy transfer rates for the PCs formed, rather than on the early/late position of the reactive transition state. A key point is that within the framework of the MURT model typical reactive trajectories do not directly address the reactive transition state but rather first become snarled and microcanonically trapped in the intermediate physisorption potential well (see Figure 1). Nine-dimensional
wavepacket simulations of gas–surface energy transfer for CH4/Ni(111) with a frozen surface lattice calculated vibrational mode-specific energy transfer efficiencies that have largely mirrored experimental vibrational efficacies. Consequently, Beck’s dynamical observation of $\eta_1(2r) \approx 0.38$ for CH4/Pt(111) may still be consistent with a late transition state if there is substantial mode-specific gas–surface energy transfer in the initial gas–surface impact or during any trapping period within the physisorption precursor well prior to reaction. On the other hand, kinetic isotope effects for methane dissociative sticking coefficients and for thermal programmed reaction of larger alkanes are consistent with C–H bond elongation defining the reaction coordinate for alkane dissociative chemisorption. As an alkane approaches the surface from the gas phase and reacts, the dynamical earliness or lateness along a C–H stretching reaction coordinate could be quite uncoupled from the evolution of the gas–surface van der Waals attraction (which finally amounts to $-E_{D0}$) given the high dimensionality of the polyatomic gas–surface reaction dynamics and energetics. In this case, the earliness (i.e., $\gamma$ near 1) of the Evans–Polanyi correlation $E_r = \gamma \Delta E + \beta \approx -\gamma E_{D0} + E_{D0}$ for a series of polyatomic alkanes would not necessarily report on the earliness or lateness of a C–H vibrational reaction coordinate for dissociative chemisorption. Beck’s measurement of $\eta_1(2r) = 0.38$ and the dynamical inference of an early barrier along a C–H stretching reaction coordinate for CH4/Pt(111) would then constitute a characterization of the reactive potential energy surface that is entirely independent of the Evans–Polanyi energetic relationship determined here.

V. Summary

The effusive molecular beam technique of measuring alkane dissociative sticking coefficients gave access to (i) quasi-thermal dissociative sticking coefficients $S_d(T)$ and (ii) nonequilibrium dissociative sticking coefficients $S_d(T_r, T)$ with $T_r \neq T$, for which gas–surface energy transfer was intimately coupled to reactivity. Dissociative sticking coefficients down to $S \sim 10^{-6}$ were measured under controlled UHV surface science conditions. A precursor-mediated microcanonical trapping (MURT) model of activated dissociative chemisorption sufficed to simulate experiments and extract transition state and gas–surface energy transfer parameters from the experimental data (see Tables 1 and 2).

Experimental threshold energies for alkane dissociative chemisorption were consistently low as compared to DFT calculated values found in the literature. Experimentally derived (lowest DFT) threshold energies for dissociative chemisorption of methane, ethane, and propane on Pt(111) were determined.

Experimental threshold energies for alkane dissociative chemisorption were consistently low as compared to DFT calculated values found in the literature. Experimentally derived (lowest DFT) threshold energies for dissociative chemisorption of methane, ethane, and propane on Pt(111) were $E_D = 50$ kJ/mol (61 kJ/mol), 34 kJ/mol (52 kJ/mol), and 20 kJ/mol (118 kJ/mol), respectively.

The linear correlation between the experimental activation energy for alkane quasi-thermal dissociative sticking and the alkane desorption energy from the physisorption well, $E_a = \gamma \Delta E + \beta \approx -\gamma E_{D0} + E_{D0}$, was interpreted as an Evans–Polanyi relation because the alkane desorption energy should approximate the van der Waals stabilization energy of the chemisorbed alkyl radical product of alkane dissociative chemisorption. The $\gamma = 0.94$ slope of the Evans–Polanyi plot indicates a late transition state for alkane dissociative chemisorption. The Evans–Polanyi correlation of $E_a$ with $E_{D0}$ is strongly suggestive that a full treatment of van der Waals interactions will be essential to achieve chemical accuracy in electronic structure theory calculations of reaction energetics for alkane activation at surfaces.