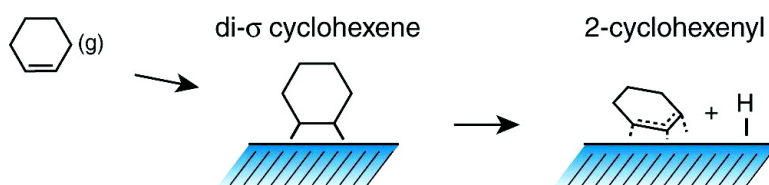


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Energetics of Cyclohexene Adsorption and Reaction on Pt(111) by Low-Temperature Microcalorimetry

Ole Lytken, Wanda Lew, Jonathan J. W. Harris, Ebbe K. Vestergaard, J. Michael Gottfried,[†] and Charles T. Campbell*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700

Received March 12, 2008; E-mail: campbell@chem.washington.edu

Abstract: The heat of adsorption and sticking probability of cyclohexene on Pt(111) were measured as a function of coverage using single-crystal adsorption calorimetry in the temperature range from 100 to 300 K. At 100 K, cyclohexene adsorbs as intact di- σ bonded cyclohexene on Pt(111), and the heat of adsorption is well described by a second-order polynomial ($130 - 47\theta - 1250\theta^2$) kJ/mol, yielding a standard enthalpy of formation of di- σ bonded cyclohexene on Pt(111) at low coverages of -135 kJ/mol and a C–Pt σ bond strength of 205 kJ/mol. At 281 K, cyclohexene dehydrogenates upon adsorption, forming adsorbed 2-cyclohexenyl ($c\text{-C}_6\text{H}_9$) and adsorbed hydrogen, and the heat of adsorption is well described by another second-order polynomial ($174 - 700\theta + 761\theta^2$) kJ/mol. This yields a standard enthalpy of formation of adsorbed 2-cyclohexenyl on Pt(111) at a low coverage of -143 kJ/mol. At coverages below 0.10 ML, the sticking probability of cyclohexene on Pt(111) is close to unity (>0.95), independent of temperature.

1. Introduction

Platinum is used to catalyze a wide range of dehydrogenation reactions. As the simplest examples of catalytic aromatization, the dehydrogenation reactions of cyclohexane and cyclohexene into benzene over platinum catalysts have been the focus of much kinetic and mechanistic study. Since Pt(111) is the most stable platinum single-crystal surface, it has been the main model catalyst used in such studies. Both cyclohexane and cyclohexene adsorb intact on Pt(111) at temperatures below 150 K.^{1–7} Above 180 K both cyclohexane and cyclohexene dehydrogenate to form a $c\text{-C}_6\text{H}_9$ intermediate,^{1,3,4,7} which above 280 K dehydrogenates further into benzene.^{1–5,7} XPS,⁵ HREELS,^{1,7} and NEXAFS⁷ studies reveal that, upon adsorption on Pt(111) at 100 K, cyclohexene exhibits only sp^3 character, suggesting a loss of its double-bond character and the formation of two new σ bonds to the platinum surface; density functional theory (DFT) calculations by Morin et al.⁸ corroborate this finding. The $c\text{-C}_6\text{H}_9$ intermediate has been found, using XPS⁵ and HREELS,^{1,4} to have partially sp^2 character. This intermediate has been suggested to be a 2-cyclohexenyl species,³ formed by removing

an allylic hydrogen from adsorbed cyclohexene. This is supported by DFT calculations by Morin et al. who find 2-cyclohexenyl to be the most stable $c\text{-C}_6\text{H}_9$ species on Pt(111).⁸ Below, we will refer to this $c\text{-C}_6\text{H}_9$ intermediate as the π -allyl. A similar intermediate has been observed for cyclohexene and cyclohexane adsorption on Pt(100).⁹ Above 280 K the π -allyl dehydrogenates further to adsorbed benzene. At elevated temperatures some benzene desorbs (if at high coverage) and the remainder dehydrogenates further via an intermediate with a 2:1 C/H ratio to eventually form graphitic carbon on Pt(111).⁵ A similar dehydrogenation pathway has been reported for the adsorption of cyclohexene on platinum nanoparticles supported on thin-film Al_2O_3 .¹⁰ The π -allyl species has also been observed during high pressure reactions of cyclohexene with Pt(111).^{11,12}

The heats of adsorption of reactants, intermediates, and products are important parameters for all catalytic systems. They reveal the thermodynamics of the elementary steps, which directly (or indirectly via Brønsted relations) influence both activity and selectivity. Traditionally, heats of adsorption are measured on single crystals using Temperature Programmed Desorption (TPD) or equilibrium measurements. However at low coverage, most hydrocarbons decompose on Pt(111) before any desorption occurs, and both TPD and equilibrium measurements fail since they are based upon reversible adsorption/desorption. At coverages close to saturation, dehydrogenation is suppressed, since no free sites exist on the surface to accommodate the dehydrogenation products, and desorption

[†] Current address: Lehrstuhl fuer Physikalische Chemie II, Universitaet Erlangen, Egerlandstr. 3, 91058 Erlangen, Germany.

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does proceed. However, as molecules desorb, free sites are created on the surface which allow the remaining molecules to dehydrogenate, and molecular desorption ceases. TPD studies of cyclohexene on Pt(111) at high coverages have been performed, but even for a fully saturated surface, less than 25% of the adsorbed cyclohexene molecules desorb intact.⁵ Hence, only information about the adsorption energies of the highest coverage states was extracted from TPD. The adsorption energy at lower coverages is not known.

The only method able to measure adsorption energies of molecules that decompose before any significant desorption occurs is a method first pioneered by D. A. King's group: single-crystal adsorption calorimetry.¹³ King's group has used calorimetry to study several systems, including the irreversible adsorption of ethylene and acetylene on nickel, palladium, and platinum single-crystal surfaces.¹⁴ In single-crystal adsorption calorimetry, heats of adsorption are measured directly as temperature changes in a thin single-crystal sample, as a molecular beam is pulsed onto the surface of the sample. We have adapted this method to allow measurements at temperatures ranging from 100 to 350 K, the use of thicker single-crystal samples (typically 1 μm), and very high temperature annealing of the samples.¹⁵ We have previously used single-crystal adsorption calorimetry to measure the heats of adsorption of benzene¹⁶ and naphthalene¹⁷ on Pt(111).

Here we present the first direct measurements of the heats of adsorption of cyclohexene as a function of coverage on Pt(111) at temperatures from 100 to 300 K. They are the first calorimetric measurements of the adsorption of any hydrocarbon on single crystal surfaces at temperatures besides room temperature. The only other calorimetry measurement of molecules adsorbing on a single crystal at cryogenic conditions was a study of O₂ adsorption on Ni(100) by King's group.¹⁸ Our results allow us to extract the heats of formation of both di- σ bonded cyclohexene and the π -allyl c-C₆H₉ intermediate on Pt(111) and to estimate average C–Pt bond energies. These heats of formation allow for a better understanding of the relative rates of competing elementary processes occurring during the dehydrogenation of cyclohexane and cyclohexene to benzene over Pt catalysts. They also provide benchmarks for assessing the accuracy of theoretical computational methods of adsorption energies of hydrocarbons and hydrocarbon fragments on the surfaces of Pt catalysts.

2. Experimental Section

The ultrahigh vacuum (UHV) chamber used in this study is pumped by a 170 L/s turbo molecular pump, a 220 L/s triode ion pump, and a liquid nitrogen cooled titanium sublimation pump (TSP) to a typical base pressure of 3×10^{-10} mbar. The chamber is equipped with X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Ion Scattering Spectroscopy (ISS), and Low-Energy Electron Diffraction (LEED). The sample was a 1 μm thick Pt(111) single crystal foil, supplied by Jacques

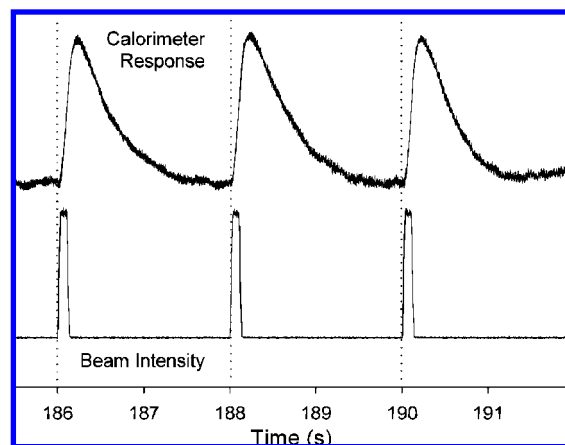


Figure 1. Raw calorimetry signal and the beam intensity (mass spectrometer signal) for cyclohexene adsorption on Pt(111) at 100 K. Each pulse is 102 ms long, consists of 2.5×10^{12} cyclohexene molecules (0.011 ML), and deposits only $\sim 0.25 \mu\text{J}$ of heat in the sample.

Chevallier at Aarhus University in Denmark. The calorimeter and vacuum chamber are described in more detail elsewhere.¹⁹

The Pt(111) sample was exposed to a pulsed molecular beam of cyclohexene; each pulse was 102 ms long and repeated every 2 s. Cyclohexene (Fluka, >99.5%) was further purified by five freeze–pump–thaw cycles. The beam was created by expanding 4 mbar of cyclohexene through a microchannel array and then collimated through a series of five liquid nitrogen cooled orifices. The diameter of the beam as it hits the sample has previously been measured to be 4.36 mm.¹⁹ Coverages are reported here in monolayers (ML) and are defined as the number of cyclohexene molecules which stuck to the surface irreversibly, independent of the actual species they then formed on the surface (which depends on temperature). We define one monolayer as the density of platinum atoms in the Pt(111) surface ($1.50 \times 10^{19} \text{ m}^{-2}$). A typical cyclohexene dose is 0.01 ML ($\sim 2 \times 10^{12}$ molecules) per pulse. A more detailed description of the experimental principles and implementation of the molecular beam can be found elsewhere.¹⁹ The flux of cyclohexene in the beam is measured by impinging the beam onto a liquid nitrogen cooled Quartz Crystal Microbalance (QCM), precovered with multilayers of cyclohexene. At 130 K (the temperature of the QCM), the sticking probability of cyclohexene onto cyclohexene multilayers is 1.00 (see below), and the flux of cyclohexene can be measured as the mass deposited onto the QCM. Calibration of the QCM has been described previously.¹⁶

The heat released from the adsorption of one cyclohexene pulse is measured by gently pressing a pyroelectric polymer ribbon against the back side of the platinum sample. The $50 \times 4 \text{ mm}^2$ ribbon was cut from a 9- μm thick, uniaxially oriented β -polyvinylidene fluoride (PVDF) polymer sheet, coated on the front and back faces with a thin Al film (purchased from Goodfellow). A temperature change in the pyroelectric polymer changes the polarization of the polymer, and an electrical charge is released into a preamplifier circuit. This discharge is detected as a voltage pulse across a 10 G Ω resistor. The raw voltage signal from the pyroelectric polymer for a couple of cyclohexene pulses can be seen in Figure 1.

A typical cyclohexene pulse releases approximately $0.25 \mu\text{J}$ of heat to the platinum sample, corresponding to an 8 mK temperature change in the sample. The estimated temperature change in the pyroelectric polymer is only 0.3 mK, based on the pyroelectric coefficient for PVDF at 100 K ($1.0 \text{ nC cm}^{-2} \text{ K}^{-1}$,²⁰). Pressing the pyroelectric polymer harder against the sample improves the heat transfer but at the risk of deforming the Pt(111) sample. At

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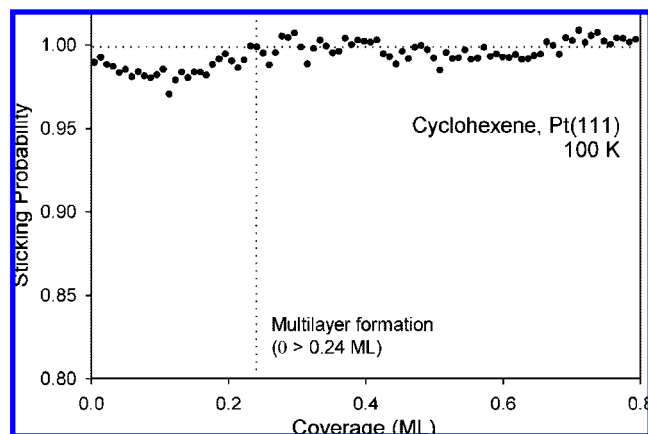


Figure 2. Sticking probability of cyclohexene on Pt(111) at 100 K. The sticking probability decreases from 0.99 on the clean surface to 0.98 at 0.10 ML, before it increases to 1.00 at coverages above 0.24 ML, remaining essentially unity (>0.98) throughout the coverage range.

100 K, we achieved a pulse-to-pulse standard deviation for the multilayer adsorption of cyclohexene of $0.0075 \mu\text{J}$, approximately 3% of the deposited energy per pulse. However, on most runs the pulse-to-pulse standard deviation was significantly higher, with an average of $0.015 \mu\text{J}$. Since PVDF loses its pyroelectric properties when heated above 350 K (unless poled), it is necessary to actively cool the PVDF ribbon and protect it from radiation during chamber bakeouts.

To reduce noise in the calorimeter, especially at low temperatures, the aluminum coating on the PVDF ribbon was removed except in a patterned area essential for measurement. This significantly reduced noise and electrical shorts across the ribbon. In combination with other changes to the detector, it also reduced the capacitance of the detector, which increased the voltage response. A description of the patterning of the PVDF ribbons and the changes to the detector can be found in ref 21.

The sensitivity of the pyroelectric polymer pressed against the backside of the platinum sample was calibrated after each experiment by depositing a known amount of energy onto the sample using a HeNe (632.8 nm) laser. The optical reflectivity of the $1\text{-}\mu\text{m}$ thin Pt(111) samples has been measured previously to be 0.76,¹⁶ slightly higher than the literature value for bulk platinum, 0.67.²² The laser power was measured using a Newport 818-SL semiconductor photodetector, which together with the optical reflectivity of the sample allowed the calculation of the energy deposited in the sample by the laser, typically about $2 \mu\text{J}$ per pulse. Just like the cyclohexene beam pulses, each laser pulse was 102 ms long, repeated every 2 s, and covered the same area of the sample.

The heat deposited by a cyclohexene pulse was determined by measuring the slope of the calorimeter voltage response versus time curve, during its initial steep rise, which transpires between 40 and 140 ms after the beam pulse starts hitting the sample (see Figure 1). This slope was compared with the corresponding slope of the laser calibration peak in the exact same time region. This method was found to yield the best signal-to-noise ratio at low temperatures (100 K), where the baseline voltage of the calorimeter was less stable than that at 300 K, probably due to temperature fluctuations in the system.

The absolute accuracy of the calorimetric heats is estimated to be better than 10%, based on the uncertainties of the optical reflectivity of the sample and the beam flux.¹⁹

The Pt(111) sample was heated radiatively (e-beam heating proved unnecessary) by placing a hot tungsten filament 1 mm

behind the sample. Since PVDF loses its pyroelectric properties if heated above 350 K, the pyroelectric ribbon was retracted and covered with a copper cup while heating the Pt sample, to protect it from radiation. The temperature of the sample during annealing was measured using an IRCon Mirage 6015-99C Infrared Thermometer (i.e., an optical pyrometer), viewing the sample through a viewport from outside the vacuum chamber.

Between experiments the sample was cleaned by 1.25 kV Ar^+ ion sputtering, annealed at 1073 K for 2 min, and exposed to 1×10^{-7} mbar O_2 at 723 K for 30 min. Treating the platinum sample in O_2 at temperatures above 723 K was found to introduce a small indium impurity (AES 404 and 410 eV). However, limiting the O_2 -treatment temperature to 723 K kept the indium impurity below the detection limit of Auger. After the oxygen treatment, the sample was allowed to cool down for 1 min in the presence of 1×10^{-7} mbar O_2 to passivate the surface with oxygen. After thermal equilibrium had been re-established throughout the calorimeter, which could take 30–60 min, the sample was flashed to 1073 K (<1 s) to remove oxygen and brought back into contact with the calorimeter. This high temperature flash (<1 s at 1073 K) was found to disturb the thermal equilibrium of the calorimeter less than a lower temperature heating for a longer time. Thermal equilibrium was usually re-established 5–10 min after flashing the sample, and an experiment was started. After this treatment the sample produced a sharp LEED pattern, and impurities were below the detection limit of Auger electron spectroscopy across the area of the platinum sample exposed to the cyclohexene beam.

The calorimeter was mounted on top of a large thermal reservoir (~ 700 g) made of OFHC copper. The thermal reservoir can be cooled with either liquid nitrogen, dry nitrogen gas, or cooling water. By passing dry nitrogen gas first through a coil of Cu tubing submerged in different low-temperature baths (i.e., a mixture of solid and liquid *p*-cymene (204 K), a mixture of ice, water, and KCl (258 K), or liquid nitrogen (77 K)), the temperatures of the detector and sample were measured by attached thermocouples and stabilized at 263, 281, and 100 K, respectively. A list of other convenient low-temperature baths can be found in ref 22.

3. Results

3.1. Sticking Probability Measurements. Sticking probabilities were measured simultaneously with calorimetric measurements, using the King and Wells method.²³ For every cyclohexene pulse, a mass spectrometer, without line-of-sight to the sample, measured the background pressure increase of cyclohexene (mass 67) in the chamber. Since cyclohexene does not stick to gold at room temperature,²⁴ a gold flag was positioned immediately in front of the sample to calibrate the mass spectrometry signal corresponding to full reflection of cyclohexene. Alternatively, at temperatures where the Pt(111) surface saturates (263, 281, and 293 K), the saturated surface can be used as a reference for full reflection. Within 2%, the amount of cyclohexene reflected off the saturated sample agreed with the amount reflected off the room-temperature gold flag. The 2% deviation is probably caused by the slight difference in position between the Pt(111) sample and the gold flag.

The sticking probability of cyclohexene for a given pulse (S_i) is defined as the fraction of cyclohexene which has not desorbed from the surface before the next cyclohexene pulse starts to hit the surface.

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$$S_i = 1 - \left(\frac{\int_{t=i t_0}^{t=(i+1)t_0} I_{Pt}(t) dt}{\int_{t=0}^{t_0} I_{Au}(t) dt} \right) \quad (1)$$

where i is the pulse number, t_0 is the time between two pulses (typically 2000 ms), t is the time measured from when the first cyclohexene pulse first hits the surface, $I_{Pt}(t)$ is the increase in cyclohexene partial pressure (mass spectrometer signal above background) at time, t , and $I_{Au}(t)$ is the increase in cyclohexene partial pressure when cyclohexene is pulsed onto the inert gold flag. We will also refer to this sticking probability as the long-time sticking probability, to distinguish it from the short-time (~ 100 ms), weighted sticking probability discussed below, which is needed to calculate adsorption energies *per mole adsorbed*.

The total coverage on the surface (θ_i) after any given pulse i , just before the next pulse hits the surface, can be calculated from the cyclohexene dose per pulse (D) and the sum of the pulse-wise sticking probabilities (S_i):

$$\theta_i = D \sum_{i=0}^{i=i} S_i \quad (2)$$

When cyclohexene is dosed onto the sample at higher temperatures, where cyclohexene multilayers are unstable, we find that weakly bound states are transiently populated at coverages close to saturation, causing a slow desorption of cyclohexene after the pulse stops. Over the course of a cyclohexene pulse cycle, heat is deposited in the sample initially as the molecules adsorb on the surface, but as the weakly bound molecules desorb after the pulse stops, some of that heat is removed. If this desorption occurs on a time scale similar to that of our heat detection (~ 100 ms), the laser calibration used, which deposits heat uniformly during 102 ms, is no longer valid, and it becomes necessary to make a correction to account for the heat removed by desorbing molecules. The method we used to approximate this extra heat correction, which is only necessary at high coverages (>0.12 ML) and high temperatures (263–293 K), is described below.

The sticking probability of cyclohexene on Pt(111) at 100 K is displayed in Figure 2. At 100 K the sticking probability of cyclohexene on Pt(111) is essentially unity (>0.98), independent of coverage. The sticking probability has a minimum of 0.98 at 0.10 ML, before reaching 1.00, as cyclohexene starts to form multilayers on the Pt(111) surface (>0.24 ML). This is consistent with molecular beam results by Jiang et al., who found the sticking probability for several small hydrocarbons (methylcyclohexane, cyclohexane, toluene, benzene) to be unity on Pt(111) at 100 K.²⁵ However, it disagrees with the sticking probability of cyclohexene on Pt(111) at 100 K of 0.21 measured by Rodriguez et al.⁵ We believe this discrepancy is caused by problems in determining the absolute cyclohexene pressure at the sample position in Rodriguez et al.'s experiments, which used only a leak valve and background pressure dosing.

The sticking probability of cyclohexene on Pt(111) at 263, 281, and 293 K is essentially unity (>0.95) at coverages below 0.10 ML (see Figure 3), indicating a precursor-mediated adsorption mechanism. A similar behavior has been observed for benzene and naphthalene adsorption on Pt(111).^{16,17} At

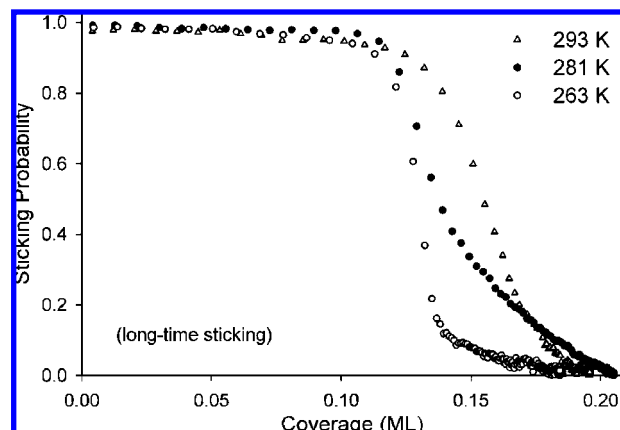


Figure 3. Long-time sticking probability of cyclohexene on Pt(111) at 263, 281, and 293 K, defined as the fraction of dosed molecules that remain on the surface until the start of the next molecular beam pulse (pulse repeat time = 2 s). From 263 to 293 K, a clear precursor-mediated adsorption behavior is evident, with the sticking probability remaining close to unity (>0.95) at coverages below 0.10 ML.

higher coverages, the sticking probability decreases abruptly with coverage for all three temperatures, until reaching saturation at approximately 0.20 ML. It seems the saturation coverage at 263 and 293 K (0.19 ML) is slightly lower than the saturation coverage at 281 K (0.21 ML). However, especially at 263 K where there is a high coverage regime (>0.15 ML) with very low sticking probability (<0.10), there is some uncertainty connected with the saturation coverage, since it involves integrating a very small value over a long time. However, the saturation coverage is expected to be higher at 281 K than at 263 K if hydrogen desorbs at 281 K but not at 263 K. If hydrogen produced from the dehydrogenation of cyclohexene to 2-cyclohexenyl is able to desorb from the surface, free sites will be created, which will allow more cyclohexene to adsorb. We do observe a rise in the background pressure of H_2 at high coverages (>0.12 ML) at 293 K; however, we never looked for hydrogen desorption at 263 or 281 K. After the surface has saturated, the background pressure of hydrogen decreases back to its original level. At 293 K a partial conversion to benzene, which takes up more space on the surface, is expected. Hence, the saturation coverage should be lower at 293 K than at 281 K.

3.2. Heat of Adsorption Measurements. Since our calorimeter can be assumed to be a constant volume calorimeter, the calorimetric heat we measure (q_{cal}) is the difference in internal energy between the initial and final state of the system (ΔU). For simplicity, we have divided the internal energy change of the system up into two internal energy changes: one for molecules adsorbing on the Pt(111) surface (ΔU_{ads}) and one for molecules reflecting off the surface (ΔU_{refl}).

$$q_{cal} = -\Delta U = -(\Delta U_{refl} + \Delta U_{ads}) \quad (3)$$

We assume molecules which do not stick to the surface of the sample but are reflected off still interact enough with the surface to become thermally equilibrated. Hence for full reflection, the initial state is a flux of molecules at the temperature of the beam nozzle, typically 293 K, and the final state is a flux of molecules at the temperature of the sample. The constant-volume molar heat capacity, C_v , for a flux of equilibrated ideal gas is $1/2R$ larger than that for a corresponding

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volume of equilibrated ideal gas, where R is the gas constant.²⁶ Hence, the internal energy change for molecules reflected off the surface becomes

$$\Delta U_{\text{refl}} = n_{\text{refl}} \int_{T_{\text{source}}}^{T_{\text{sample}}} \left(C_v + \frac{1}{2}R \right) dT \quad (4)$$

where n_{refl} is the number of moles of reflected molecules.

The internal energy change when molecules adsorb on the surface of the sample, ΔU_{ads} , can be written as a sum of three terms: (1) the standard internal energy change for an equilibrated volume of gas at the temperature of the surface and 1 bar pressure adsorbing on the surface (ΔU°); (2) a term $\frac{1}{2}RT_{\text{source}}$ per mole associated with the internal energy difference between a flux of gas and a volume of gas at 1 bar pressure, both at the temperature of the source; and (3) the internal energy change associated with cooling a volume of molecules from the temperature of the molecular beam source to the temperature of the sample. (For ideal gases, the internal energy is independent of pressure, and we only choose 1 bar here so that we can discuss “standard” thermodynamic properties, i.e., at 1 bar.) Thus

$$\Delta U_{\text{ads}} = \Delta U^\circ + n_{\text{ads}} \left(\frac{1}{2}RT_{\text{source}} + \int_{T_{\text{source}}}^{T_{\text{sample}}} C_v dT \right) \quad (5)$$

where n_{ads} is the number of moles of adsorbing molecules.

The standard enthalpy of adsorption at the sample temperature is equal to the standard change in internal energy plus the pressure–volume work ($\Delta n_{\text{gas}}RT_{\text{sample}}$) included in the enthalpy term:

$$\Delta H^\circ = \Delta U^\circ + \Delta n_{\text{gas}}RT_{\text{sample}} = \Delta U^\circ - n_{\text{ads}}RT_{\text{sample}} \quad (6)$$

Combining eqs 3–6, we can write the negative of the standard enthalpy of adsorption ($-\Delta H^\circ$) as the measured calorimetric heat (q_{cal}) plus two corrections associated with reflection and adsorption:

$$K_{\text{refl}} = \int_{T_{\text{source}}}^{T_{\text{sample}}} \left(C_v + \frac{1}{2}R \right) dT \quad (7)$$

$$K_{\text{ads}} = \int_{T_{\text{source}}}^{T_{\text{sample}}} C_v dT + \frac{1}{2}RT_{\text{source}} + RT_{\text{sample}} \quad (8)$$

Thus, the standard molar enthalpy of adsorption ($\Delta H^\circ/n_{\text{ads}}$) can be written as

$$\frac{\Delta H^\circ}{n_{\text{ads}}} = \frac{-q_{\text{cal}} - n_{\text{refl}}K_{\text{refl}} - n_{\text{ads}}K_{\text{ads}}}{n_{\text{ads}}} \quad (9)$$

Throughout the text we will use the term *heat of adsorption*, which we define here as the negative of the differential standard molar enthalpy of adsorption ($-\Delta H^\circ/n_{\text{ads}}$), at the temperature of the sample.

Using heat capacities calculated by Dorofeeva et al. for gas phase cyclohexene in the temperature range 100–1500 K,²⁷ the correction terms K_{refl} and K_{ads} , for a beam temperature of 293 K and a sample temperature of 100 K, become -13 and -10 kJ/mol, respectively.

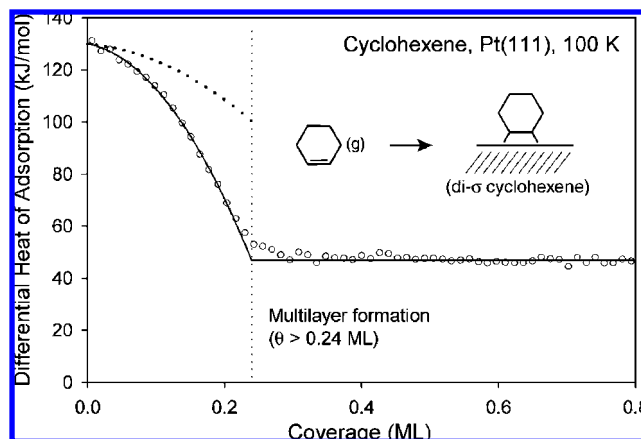


Figure 4. Differential heat of adsorption of cyclohexene on Pt(111) at 100 K, where di- σ bonded cyclohexene is initially formed. The solid line represents two separate fits to the data in two separate regions. In region one (<0.24 ML) a second-order polynomial ($130 - 47\theta - 1250\theta^2$) kJ/mol has been chosen to fit the data, yielding an initial heat of adsorption of 130 kJ/mol. In region two (>0.24 ML) the heat of adsorption remains constant at 47 kJ/mol. The bold dotted line represents the integral heat of adsorption, based on the polynomial fit.

Figure 4 shows the resulting heat of adsorption of cyclohexene on Pt(111) at 100 K versus coverage. Previous studies of cyclohexene on Pt(111) have identified the submonolayer adsorbed species at 100 K to be di- σ bonded cyclohexene (see above). Hence, the heat of adsorption of cyclohexene below 0.2 ML in Figure 4 should represent the heat of adsorption of di- σ bonded cyclohexene on Pt(111).

We have divided the heat of adsorption at 100 K into two regions: The multilayer region (>0.24 ML), where the heat of adsorption is constant (47 kJ/mol), and the submonolayer region (<0.24 ML), where the heat of adsorption is well described by a second-order polynomial ($130 - 47\theta - 1250\theta^2$) kJ/mol, yielding an initial heat of adsorption of 130 kJ/mol. Using the low-coverage limit of this fit (130 kJ/mol) and the standard enthalpy of formation of gas phase cyclohexene at 298 K (-5 kJ/mol²²), the standard enthalpy of formation of intact, di- σ bonded cyclohexene on Pt(111) can be calculated to be -135 kJ/mol. (These numbers are not corrected for the change in enthalpy with temperature.)

The onset of multilayer formation agrees well with a previous TPD study by Rodriguez et al.,⁵ which found multilayer formation to begin at 0.23–0.27 ML. Using first-order Redhead analysis of the desorption peak temperature of the multilayer and assuming a pre-exponential factor of 10^{13} s⁻¹, Rodriguez et al. found a multilayer desorption energy of cyclohexene of 38 kJ/mol. However, Tait et al.^{28,29} have found that pre-exponential factors for desorption of n -alkanes may be significantly higher than 10^{13} s⁻¹. By assuming that the prefactor for desorption scales exponentially with the standard entropy (S°) of the gas phase molecule, we can estimate the desorption prefactor for cyclohexene ($S^\circ = 310.5$ J/K mol²⁷) to be similar to the prefactor measured by Tait et al. for n -butane ($S^\circ = 309.6$ J/K mol³⁰). For n -butane Tait et al. find desorption prefactors in the range $10^{14.7} - 10^{15.7}$ s⁻¹. Reanalyzing Rodriguez et al.’s

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cyclohexene TPD data using a pre-exponential factor for desorption on 10^{15} s^{-1} instead of 10^{13} s^{-1} , we find a multilayer desorption energy for cyclohexene of 44 kJ/mol. In another TPD study by Syomin et al. the multilayer desorption energy of cyclohexene was found using an Arrhenius plot to be 42 kJ/mol;²⁴ however, the value of the pre-exponential factor was not given. Both values are in good agreement with our heat of adsorption of 47 kJ/mol.

From bulk calorimetric measurements of condensed cyclohexene,^{31,32} the standard heat of vaporization of cyclohexene,²² and calculations of the heat capacity of cyclohexene gas,²⁷ we estimate the standard heat of sublimation of bulk cyclohexene at 100 K to be 51 kJ/mol, in good agreement with our value (47 kJ/mol). The small deviation between this value and the heat of adsorption we measure for multilayer formation may come from uncertainties in both the calculated and the measured values; the formation of a less stable solid cyclohexene phase, as molecules are deposited onto the 100 K cold Pt surface, is also a possibility, especially in the short time scale (~ 100 ms) of the heat measurement.

Above 180 K, adsorbed cyclohexene dehydrogenates and forms a conjugated allylic cyclohexenyl (π -allyl-c-C₆H₉) plus one hydrogen adatom (see Introduction). At low coverages, this π -allyl remains stable below 280 K.^{3,33} Above 280 K, the π -allyl dehydrogenates further, forming adsorbed benzene (see above). To ensure accurate measurements of the heat of adsorption in the π -allyl temperature range, we have chosen to operate in the high temperature region of the π -allyl temperature range (263 and 281 K). This ensures a fast dehydrogenation of cyclohexene into the π -allyl. Furthermore, we are not able to directly measure the temperature of the thin platinum sample. Instead, we measure the temperature of the holder of the pyroelectric ribbon, which is in thermal contact with the sample holder. This makes the temperature we measure an upper limit on the temperature of the sample, and it is possible the actual temperature of the sample may be 10–20 K below what we measure.

The heats of adsorption at 263 and 281 K are shown in Figures 5 and 6, respectively, and should both represent the heat of adsorption of cyclohexene forming the π -allyl plus one adsorbed hydrogen adatom. The heat of adsorption at 281 K is well described by a second-order polynomial ($174 - 700\theta + 761\theta^2$) kJ/mol, with an initial heat of adsorption of 174 kJ/mol. We have included the 281 K polynomial fit in Figure 5 with the 263 K heat of adsorption. It is apparent that the heats of adsorption at 263 and 281 K are very similar, with the heat of adsorption at 263 K being slightly lower. However, only two experiments were performed at 263 K compared to five at 281 K. We therefore expect a higher uncertainty on the 263 K results, enough to explain the approximately 5–10 kJ/mol difference.

The heat of adsorption at 293 K is shown in Figure 7. At 293 K, we expect at least a partial conversion to benzene (see above), and we do observe a higher heat of adsorption compared to 281 K throughout the coverage range. At 293 K a second-order polynomial did not yield a good fit and we had to use a fourth-order polynomial ($202 - 1650\theta + 16412\theta^2 - 93754\theta^3 + 208902\theta^4$) kJ/mol, giving an initial heat of adsorption of 202 kJ/mol.

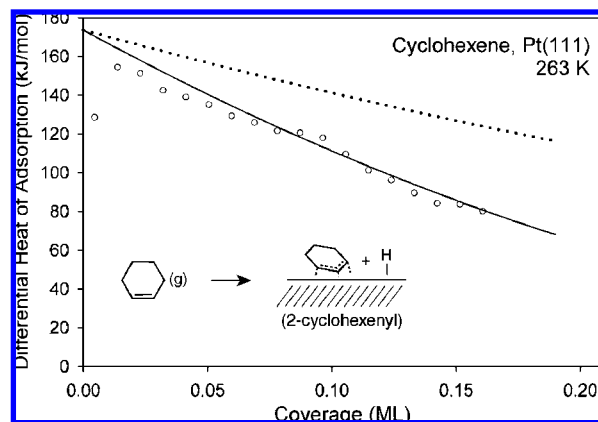


Figure 5. Differential heat of adsorption of cyclohexene on Pt(111) at 263 K, where it forms adsorbed π -allyl-c-C₆H₉ (2-cyclohexenyl). The solid line is the fit to the heat of adsorption data at 281 K, taken from Figure 6 below ($174 - 700\theta + 761\theta^2$) kJ/mol, showing that the behavior is essentially the same from 263 to 281 K. The bold dotted line represents the integral heat of adsorption, based on the polynomial fit. Some uncertainty is associated with values above 0.12 ML, due to reversible adsorption (see section 3.3).

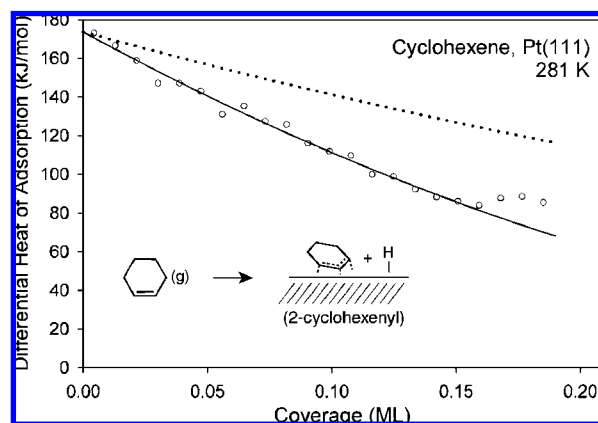


Figure 6. Differential heat of adsorption of cyclohexene on Pt(111) at 281 K, where it forms π -allyl-c-C₆H₉ (2-cyclohexenyl). The solid line is a second-order polynomial fit to the data ($174 - 700\theta + 761\theta^2$) kJ/mol, yielding an initial heat of adsorption of 174 kJ/mol. The bold dotted line represents the integral heat of adsorption, based on the polynomial fit. Some uncertainty is associated with values above 0.12 ML, due to reversible adsorption (see section 3.3).

The heat of adsorption of cyclohexene on Pt(111) at high coverages has been measured previously by Rodriguez et al. using TPD.⁵ Four desorption peaks were observed: α , β , γ , and λ . Using Redhead analysis and assuming a pre-exponential factor for desorption of 10^{13} s^{-1} , Rodriguez et al. found the corresponding desorption energies to be 38, 46, 63, and 75 kJ/mol. Reanalyzing Rodriguez et al.'s data, using a more accurate estimate of the pre-exponential factor for desorption of cyclohexene (10^{15} s^{-1}) (see above), we find desorption energies of 44 kJ/mol (>0.27 ML), 54 kJ/mol ($0.23 \text{ ML} < \theta < 0.27 \text{ ML}$), 73 kJ/mol ($0.19 \text{ ML} < \theta < 0.23 \text{ ML}$), and 87 kJ/mol ($0.17 \text{ ML} < \theta < 0.19 \text{ ML}$). These energies and coverage ranges have been included in Figure 8 together with our calorimetric data. The overlap is not perfect; however, the accuracy is within what can reasonably be expected from a very simple analysis (first-order Redhead) of very complicated data (four overlapping desorption peaks), with several competing reactions (desorption and dehydrogenation). It stresses the importance of direct

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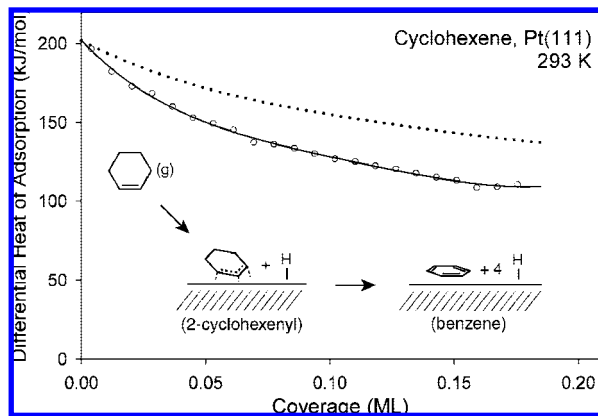


Figure 7. Differential heat of adsorption of cyclohexene on Pt(111) at 293 K, where a partial conversion from π -allyl- c - C_6H_9 (2-cyclohexenyl) to benzene is expected. The solid line is a fourth-order polynomial fit ($202 - 1650\theta + 16412\theta^2 - 93754\theta^3 + 208902\theta^4$) kJ/mol, giving an initial heat of adsorption of 202 kJ/mol. The bold dotted line represents the integral heat of adsorption, based on the polynomial fit. Some uncertainty is associated with values above 0.12 ML, due to reversible adsorption (see section 3.3).

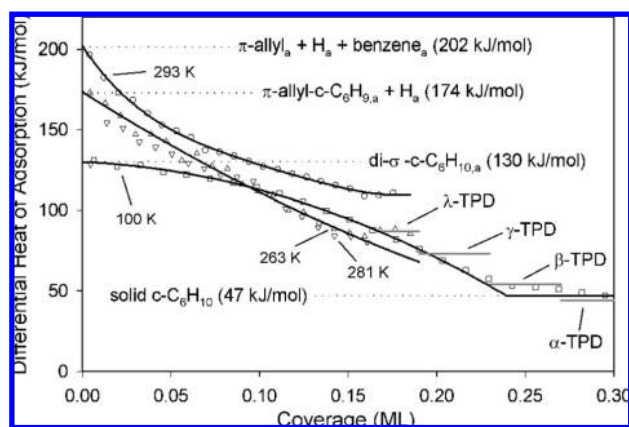


Figure 8. Differential heat of adsorption of cyclohexene on Pt(111) in the temperature range 100–293 K. Above 0.10 ML, the heats of adsorption at 100 and 281 K become very similar, indicating that the same species may be formed on the surface at both temperatures in that coverage range. The solid lines are fits to the heats of adsorption described in Figures 4–7. Shown in the figure are also high-coverage adsorption energy estimates based on Rodriguez et al.'s TPD study⁵ (see text).

calorimetric measurements for determining accurate adsorption energies of such systems.

3.3. Short-Time, Weighted Sticking Probability (S_w). The Experimental Section described how the sensitivity of the heat detector is calibrated using a pulsed laser, depositing a known amount of heat in the sample. This is a good calibration, when there is no delay between the molecular pulse and the deposited heat; e.g., heat is deposited instantly when molecules adsorb on the surface. However, above 250 K and at high coverages transient adsorption/desorption occurs. Initially, molecules adsorb on the surface and deposit heat, with no delay between the molecular pulse and the deposited heat. However, some of those molecules then later desorb, removing heat from the sample. If there is a significant delay between the molecular pulse and this removal of heat, the line shape of the heat signal will change, in which case the laser calibration described in the Experimental Section is no longer accurate.

If this transient desorption happens on a time scale much faster than that of our heat detection ($\ll 100$ ms), the heat signal

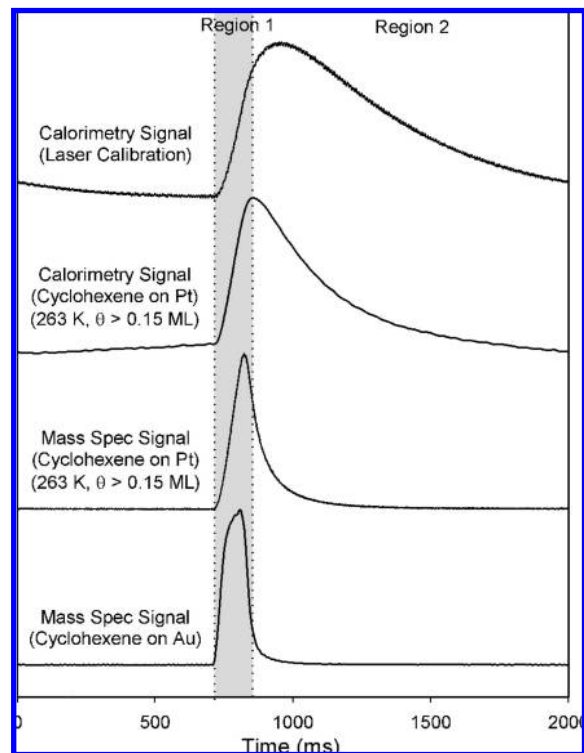


Figure 9. Calorimetry and mass spectrometer signals for cyclohexene adsorption on Pt(111) in a region with a significant amount of transient desorption (263 K, >0.15 ML). Notice the line shape differences in the calorimetry signal between adsorption and laser calibration, and in the mass spectrometer signal between desorption from the platinum sample and desorption from the gold flag. The slow desorption from the platinum sample causes a delayed removal of heat, making the calorimetry peak sharper for adsorption than for laser calibration. All traces are normalized averages of 50 or more pulses. Both the calorimetry signal and the desorption from the gold flag have been low-pass filtered for presentational purposes.

is the same as if the molecules were simply reflected, and no correction needs to be made. If desorption occurs on a time scale that is much slower than our heat detection time (i.e., $\gg 100$ ms), we can neglect the desorption for heat purposes. However, if molecules which adsorb during a gas pulse start to desorb on a time scale similar to that of our heat detection (≈ 100 ms), the delayed removal of heat will affect the measurement, and it becomes necessary to make a correction to account for the heat removed by desorbing molecules. Using a mass spectrometer, we measure the sticking probability of cyclohexene during each pulse, by measuring the background pressure rise of cyclohexene in the chamber caused by desorption/reflection of cyclohexene from the sample. Hence, we can directly observe any delayed desorption by comparing the shape of the background pressure rise when molecules are pulsed onto the sample with that of a corresponding background pressure rise when molecules are pulsed onto an inert gold flag. We use the gold flag as a reference for instant desorption/reflection, instead of the intrinsic intensity of the direct beam, because cyclohexene has a lifetime in the background of the chamber. Hence, the gold flag reference will have a small delay compared to the intrinsic intensity of the direct beam. The background pressure rise of cyclohexene when pulsed onto an inert gold flag at 300 K can be seen in Figure 9. Because of the lifetime of cyclohexene in the chamber, most likely caused by adsorption on the chamber walls, the mass spectrometer line shape is not a perfect trapezoid. For comparison, the intrinsic intensity of the beam can be seen in Figure 1. Included in Figure 9 are also the background cyclohexene

pressure rise for temperature and coverage with a large amount of transient desorption (263 K, >0.15 ML), the shape of the calorimetry signal for that temperature and coverage, and the shape of the calorimetry signal for a laser calibration pulse.

We measure the amount of heat deposited by measuring the slope of the calorimetry pulse during the initial steep rise, typically 40–140 ms after the pulse hits the sample. There is a delay between the heat deposited in the sample and the calorimetry signal, because the thermal contact between the Pt(111) sample and the pyroelectric polymer is not great.

Since the calorimetry signal after the initial steep rise is not used for calculating the amount of heat deposited, any desorption happening after that point in time (140 ms) should be neglected for heat purposes. Desorption happening during the first 140 ms will affect the heat we measure. However, since there is a delay between heat deposited in the sample and the calorimetry signal, desorption happening early during those 140 ms will affect the measured heat more than desorption happening late during the 140 ms. Since we do not know the exact relative weight to give events happening inside the 140 ms window, we will assume a simple linear weight. Desorption happening at $t = 0$ ms will be given a weight of one; they are to be considered fully desorbed for heat purposes. Desorption happening at $t = 140$ ms and longer will be given a weight of zero; they are to be considered fully adsorbed for heat purposes. Anything in between will be considered fractionally desorbed for heat purposes. Hence, we now introduce the weight function $w_i(t)$:

$$w_i(t) = 1 - \frac{t - i \cdot t_0}{t_1}$$

where t is the time from when the first pulse hits the surface, t_0 is the time between two pulses (typically 2000 ms), t_1 is the end of the initial steep rise (typically 140 ms), and i is the pulse number. We will now introduce a weighted sticking probability (S_{wi}), which is the fraction of a pulse which is to be considered adsorbed for heat purposes:

$$S_{w_i} = \left(\frac{\int_{t=i \cdot t_0}^{t=i \cdot t_0 + t_1} I_{Pt}(t) \cdot w_i(t) dt}{\int_{t=t_0} I_{Au}(t) \cdot w_0(t) dt} \right)$$

Here, $I_{Pt}(t)$ is the background pressure rise of cyclohexene when cyclohexene is pulsed onto the Pt(111) sample, and $I_{Au}(t)$ is the background pressure rise when cyclohexene is pulsed onto an inert gold flag at 300 K.

We have plotted these weighted sticking probabilities used to calculate the deposited heats *per mole* at 263, 281, and 293 K in Figure 10. At 293 K the difference between the sticking probability (S) and the weighted sticking probability (S_w) is quite small even at high coverages, since desorption from the transiently adsorbed state is almost instantaneous at 293 K. However as the temperature of the sample is reduced, the lifetime of this transiently adsorbed state increases, and at 281 K there is a significant difference between the sticking probability and the weighted sticking probability at high coverages. At 263 K the difference is even larger at high coverages. At 263 K and 0.17 ML the sticking probability is only 0.05, whereas the weighted sticking probability is 0.70. Hence, at 263 K and 0.17 ML the accuracy of the reported heat of adsorption depends critically on the accuracy of the weighted sticking

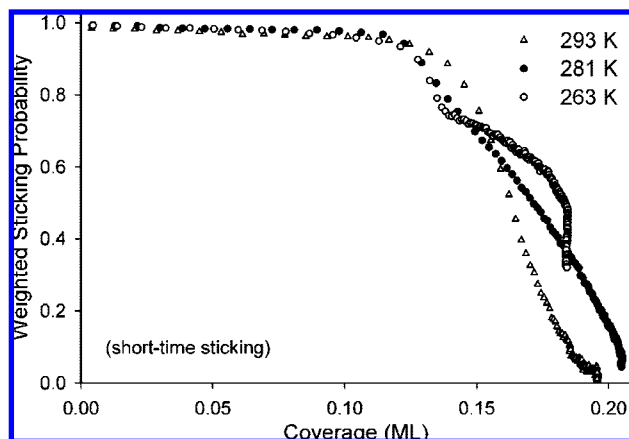


Figure 10. Weighted, short-time sticking probability (S_w) of cyclohexene on Pt(111) versus coverage from 263 to 293 K. As described in the text, S_w is used for calculating the heats of adsorption *per mole adsorbed* and roughly equals the fraction of pulsed molecules that remain on the surface for the short time of the heat signal measurement (~ 100 ms). The corresponding long-time sticking probability (S), which was used to calculate coverages, was reported in Figure 3. At 293 K, the difference between the long-time sticking probability and this weighted, short-time sticking probability is quite small, even at high coverages (>0.15 ML). However, at 281 K, the difference grows bigger, and at 263 K, this weighted sticking probability is much larger than the long-time sticking probability above 0.12 ML, due to reversibly adsorbed species with lifetimes longer than 100 ms but shorter than 2000 ms.

probability correction. The weighted sticking probability was only necessary for calculating the heat of adsorption *per mole adsorbed*, not for calculating the coverage of cyclohexene on the surface. The coverage was always calculated using eqs 1 and 2 in the Results section.

Although this method is a rough approximation, it allows us to address conditions where a moderate amount of transient desorption occurs. However, the validity of this method is questionable whenever there is a large fraction of transient desorption, such as the adsorption of cyclohexene on Pt(111) at 263 K at coverages above 0.15 ML; see Figure 10. This correction will have no influence at coverages and temperatures where no transient desorption occurs, such as adsorption at 100 K and adsorption at coverages below 0.12 ML at all higher temperatures studied here.

4. Discussion

Recently two groups have published DFT calculations of cyclohexene adsorbed on Pt(111): Morin et al.⁸ and Saeys et al.³⁴ Morin et al. used a $p(3 \times 3)$, four-layer periodic slab corresponding to a cyclohexene coverage of 0.11 ML. They calculated the adsorption energy for di- σ bonded cyclohexene at $1/9$ ML to be 112 kJ/mol, in good agreement with our experimental value for the integral heat of adsorption of di- σ bonded cyclohexene at 0.11 ML (122 kJ/mol). The most stable adsorption structure was found to be a di- σ boat structure with the methylene groups bending down toward the surface.

Saeys et al.³⁴ used a two-layer 22 atom platinum cluster with a (111) surface. The study suggests that the most stable cyclohexene configuration on the surface was a di- σ boat conformation with the methylene groups bending away from the surface and with an adsorption energy of 81 kJ/mol. The

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boat conformation was considered more stable than the chair because the conformation allows the vinylic hydrogens to be eclipsed, allowing perfect di- σ adsorption. This adsorption energy needs to be compared with the energy measured in the limit of zero coverage, 130 kJ/mol, so the calculated value is 49 kJ/mol lower than our experimental value. It is possible that Saeys et al. used a too small cluster for their calculations. In an older, very comprehensive study of hydrocarbon adsorption energies on Pt(111), Koel et al.³⁵ used a quasiempirical valence bond (QVB) scheme and calculated an adsorption energy of di- σ bonded cyclohexene on Pt(111) of 71 kJ/mol, also significantly smaller than our value.

Strictly speaking, the adsorption energy calculated by DFT is the negative internal energy of adsorption ($-\Delta U$) at 0 K. Hence, to make a true comparison to the heat of adsorption ($-\Delta H$), the adsorption energy has to be corrected for temperature (using heat capacities) and converted into an enthalpy difference. Converting an internal energy change into an enthalpy change is a straightforward addition of $-n_{\text{ads}}RT_{\text{sample}}$; see eq 6. However, correcting for the temperature difference requires knowledge of the constant volume heat capacity (C_v) of both gas phase cyclohexene and the adsorbed species over the full range from 0 K up to T_{sample} , and the heat capacity of the adsorbed species is not known. Assuming cyclohexene loses only its three translational degrees of freedom upon adsorption, the heat capacity of the adsorbed species should be $3/2R$ smaller than the heat capacity of gas phase cyclohexene, so that the ΔU of adsorption is larger than that at 0 K by $3/2RT_{\text{sample}}$. Combining these two terms, the heat (negative enthalpy) of adsorption at a temperature T_{sample} can be calculated to be $5/2RT_{\text{sample}}$ larger than the adsorption energy at 0 K. At 100 K this correction is 2 kJ/mol, and at 280 K it is 6 kJ/mol.

The similar heat of adsorption measured at both 263 and 281 K suggests that the same species are formed at both temperatures. At low to moderate coverages, the products are known to be π -allyl plus one adsorbed hydrogen adatom (see above). At low coverages, the π -allyl has been observed to be stable below 280 K.^{3,33} Above 280 K, the π -allyl is expected to dehydrogenate further, forming adsorbed benzene. This means a slow conversion from π -allyl to adsorbed benzene is very likely at 281 K. However, we believe that on the time scale of our heat detection (100 ms), which is much faster than the time scale in Pettiette-Hall et al.'s experiments (30 s), only π -allyl plus adsorbed hydrogen is formed on the Pt(111) surface. We believe the small deviation between the measured heats of adsorption at 263 and 281 K is caused by the fewer number of experiments averaged at 263 K: two experiments at 263 K vs five experiments at 281 K.

A more useful number than the heat of adsorption for cyclohexene forming π -allyl and hydrogen is the enthalpy of formation of the π -allyl on Pt(111), which may be extracted knowing the adsorption energy of hydrogen on Pt(111). The adsorption energy of hydrogen on Pt(111) has been the subject of some discussion in the literature, with adsorption energies as low as 39 kJ/mol H₂ being reported.^{36,37} However, most studies agree on an adsorption energy in the range 65–79 kJ/mol,^{38–44} with an average value of 72 kJ/mol. Using that

number, the standard enthalpy of formation of cyclohexene gas (-5 kJ/mol),²² and our initial heat of adsorption of cyclohexene on Pt(111) at 281 K (174 kJ/mol), the standard enthalpy of formation for π -allyl-c-C₆H₉ adsorbed on Pt(111) is calculated to be -143 kJ/mol at 263–281 K.

Morin et al. have performed DFT calculations on several possible intermediates in the dehydrogenation of cyclohexene to benzene on Pt(111), including the π -allyl.⁸ Of three possible C₆H₉ intermediates, Morin et al. find 2-cyclohexenyl (π -allyl) to be the most stable, with an adsorption energy, relative to gas phase benzene and gas phase hydrogen, of 179 kJ/mol. They find the most stable adsorption site to be an hcp site, forming a triple- σ bonded species. However, experimental XPS C(1s) binding energies^{5,10} and HREELS^{1,2,4} suggest that the π -allyl has partially sp² character and, thus, at least partial π bonding to the platinum surface. However, Morin et al. find the adsorption energy of the hcp triple- σ species and the bridge $\sigma\pi$ species to differ by only 6 kJ/mol, within the uncertainty of their calculation. Using the standard enthalpy of formation of benzene gas (83 kJ/mol),²² the standard enthalpy of formation of cyclohexene gas (-5 kJ/mol),²² and the adsorption energy of H₂ on Pt(111) calculated by Morin et al. (90 kJ/mol),⁸ we can use Morin et al.'s adsorption energy of the π -allyl to calculate the adsorption energy for gas phase cyclohexene forming the π -allyl and adsorbed hydrogen to be 146 kJ/mol. This heat of adsorption should be compared with the integral heat of adsorption we find for cyclohexene adsorption at 281 K and 0.11 ML (139 kJ/mol). This is in excellent agreement, especially considering we have hydrogen present on the surface together with the π -allyl, which could affect the heat of adsorption. It should also be noted that the difference would have been even smaller had we used the experimental adsorption energy of hydrogen (72 kJ/mol) instead of the calculated value (90 kJ/mol).

However, using the same DFT methods as mentioned above, Morin et al. significantly underestimate the heat of adsorption of benzene on Pt(111). Whereas Morin et al. calculate the integral heat of adsorption at 0.11 ML to be 87 kJ/mol for benzene,⁸ our recent microcalorimetric measurements with this same apparatus yield 165 kJ/mol for the same coverage.¹⁶ A similar discrepancy ($\sim 50\%$) has been found for naphthalene adsorption on Pt(111). This is at least partially due to the relatively larger role played by London dispersion forces in benzene and naphthalene adsorption,¹⁷ since these are not well treated by DFT. The conclusion is that DFT is capable of calculating very reliable adsorption energies for hydrocarbons with bonding dominated by strong Pt–C σ -bonds; however, weaker π -bonded systems, such as benzene on Pt(111), remain a challenge. Using a quasiempirical valence bond (QVB) scheme, Koel et al.³⁵ calculated the energy difference between gas-phase cyclohexene and the π -allyl plus adsorbed hydrogen to be 205 kJ/mol, significantly higher than our measured value of 174 kJ/mol.

The initial heat of adsorption of cyclohexene at 293 K is 202 kJ/mol. We can compare this value with the heat of adsorption

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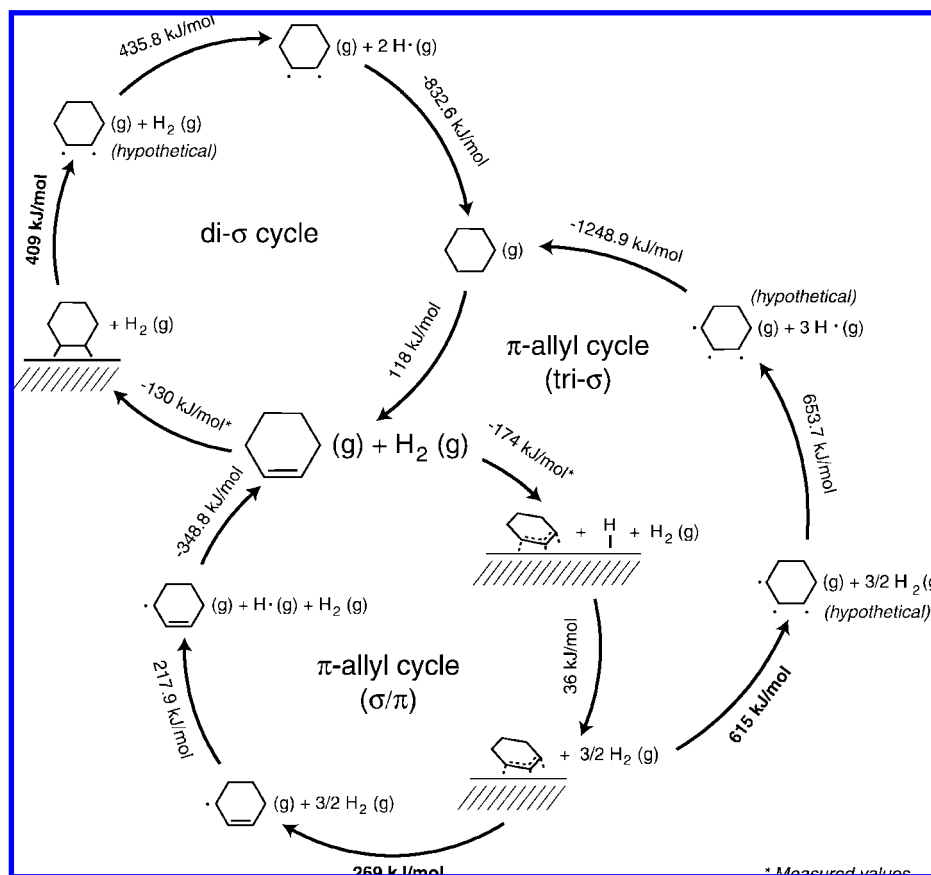


Figure 11. Three cycles used to calculate the average C–Pt bond strength for di- σ bonded cyclohexene and π -allyl-c-C₆H₉ on Pt(111). Two different cycles are shown for the π -allyl: one assuming a tri- σ bonded species and one assuming a σ/π bonded species. The values indicated with an * are the standard enthalpies of adsorption from the present study, and the values in bold are adsorption energies, relative to the corresponding gas-phase radicals, calculated by setting the sum of the enthalpies for that cycle equal to zero. The di- and triradicals are hypothetical species wherein the energy costs for removing the second and third hydrogen were assumed to be identical to that for removing the first hydrogen, so that any radical–radical interactions between neighboring carbon atoms are neglected.

expected if the cyclohexene completely converts to adsorbed benzene plus adsorbed hydrogen. To do that, we used the standard enthalpy of formation of benzene gas (83 kJ/mol)²² and cyclohexene gas (–5 kJ/mol),²² the adsorption energy of H₂ (72 kJ/mol),^{38–44} and the heat of adsorption of benzene (197 kJ/mol).¹⁶ This yields an expected initial heat of adsorption of 253 kJ/mol, significantly higher than our measured value (202 kJ/mol). Hence, we believe that, at least on the time scale of our heat detection (100 ms), only a partial conversion of π -allyl to adsorbed benzene is taking place at 293 K. During the time scale of an entire experiment (2 min to approach saturation), a more complete conversion to benzene may take place, and most adsorbed hydrogen most likely desorbs, producing a surface with mostly adsorbed benzene and little hydrogen. Using the mass spectrometer we did observe a background pressure increase of H₂ at high coverages at 293 K. As the Pt(111) surface saturated, the hydrogen background pressure returned to its normal level. However, we were unable to quantify the amount of hydrogen desorbing from the surface. We also performed experiments wherein we monitored the cyclohexane and benzene background pressures, but we did not observe any desorption of either cyclohexane or benzene at 293 K. The saturation coverage of benzene on Pt(111) at 298 K has previously been measured to be approximately 0.15 ML.^{45,46} For a complete conversion of cyclohexene to benzene we would therefore expect

the surface to saturate at approximately 0.15 ML. The higher observed saturation coverage of 0.19 ML (see Figure 3) indicates that the conversion to benzene is only partial at 293 K, even on the time scale of an entire experiment (2 min).

4.2. Carbon–Platinum Bond Strengths. Three thermodynamic cycles were used to calculate the average C–Pt bond strength for di- σ bonded cyclohexene and the π -allyl on Pt(111), as shown in Figure 11. Two different cycles are shown for the π -allyl: one assuming a tri- σ bonded species and one assuming a σ/π bonded species. The values indicated with an * are the standard enthalpies of adsorption measured in the present study. The values in bold are adsorption energies, relative to the corresponding gas-phase radicals, calculated by setting the sum of the enthalpies for that cycle equal to zero. The adsorption energy of hydrogen on Pt(111) is an average of experimental values, 72 kJ/mol.^{38–44} All other values were taken from tables of gas phase enthalpies of formation and bond dissociation energies at 298 K.²² In the absence of a tabulated value for the C–H bond strength for an allylic hydrogen in cyclohexene gas, the C–H bond strength of an allylic hydrogen in 1-pentene (348.8 kJ/mol²²) was used instead. The di- and triradicals are hypothetical species wherein the bond strengths for removing the second and third hydrogen were assumed to be identical to that for removing the first hydrogen (416.3 kJ/mol²²), so that any radical–radical interactions between neighboring carbon

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atoms are neglected. Note that these are the most appropriate species to use in such cycles to accurately estimate the average C–Pt bond energies.

Using the di- σ cycle in Figure 11, the adsorption energy of di- σ -bonded cyclohexene, relative to the hypothetical gas-phase diradical, is 409 kJ/mol, yielding a C–Pt σ bond strength of 205 kJ/mol for di- σ bonded cyclohexene on Pt(111). This average C–Pt σ bond energy is slightly weaker than the values found by King's group for di- σ -bonded ethylene on Pt(110)-(1 \times 2) (235 kJ/mol)⁴⁷ and Pt(100)-(1 \times 1) (253 kJ/mol).⁴⁸ However, King et al. extracted the C–Pt σ bond strength of di- σ bonded ethylene based on the heat of adsorption of ethylene at high coverages,^{47,48} where a significant amount of adsorbate–adsorbate repulsion is expected. Hence, the C–Pt σ bond strength of di- σ bonded ethylene at low coverages is expected to be even higher than 235–253 kJ/mol. The lower C–Pt σ bond strength for cyclohexene compared to ethylene may be caused by the large amount of strain in the adsorbed di- σ bonded cyclohexene molecule, relative to gas phase cyclohexene,³⁴ or the lower degree of coordinative unsaturation of the platinum atoms on this (111) face compared to (110) and (100). A small part of this difference is also expected because adsorbed cyclohexene involves C–Pt bonds to secondary carbon atoms and not to primary carbon atoms as in adsorbed ethylene. For organometallic compounds, the bond strength between a ligand and the metal center has been found to scale linearly (with a slope of one) with the bond strength between the ligand and hydrogen.^{49,50} Hence, even neglecting all other effects, the difference in C–Pt bond strength between adsorbed cyclohexene and adsorbed ethylene should be equal to the difference in C–H bond strength between cyclohexane (416.3 kJ/mol) and ethane (420.5 kJ/mol),²² 8 kJ/mol.

For the cycles in Figure 9, we assume the heat of adsorption of di- σ bonded cyclohexene at 298 K to be identical to the heat of adsorption we measure at 100 K. To be able to correct for the temperature difference, it is necessary to know the heat capacity of cyclohexene gas, which is known,²⁷ and the heat capacity of adsorbed cyclohexene, which is unknown. However, assuming the heat capacity of the adsorbed species to be similar to the heat capacity of pure condensed phase cyclohexene^{31,32} (which may be a questionable approximation), we can estimate the heat of adsorption at 298 K to be approximately 10 kJ/mol smaller than the heat of adsorption we measure at 100 K, yielding a Pt–C bond strength of 200 kJ/mol instead of 205 kJ/mol. However, the accuracy of this estimation is somewhat uncertain. For the adsorption measurements at 281 K the temperature difference between 281 and 298 K is much smaller, and hence, such a correction becomes negligible.

Since the π -allyl is believed to be bonded to the surface in a σ/π mode rather than a tri- σ mode, the total bond strength is calculated relative to the gas phase 2-cyclohexenyl monoradical. This yields a total bond strength of 269 kJ/mol (see the π -allyl cycle (σ/π) in Figure 11). This bond strength can be compared to the expected bond strength for one C–Pt σ bond plus one C–Pt π bond. Using the average C–Pt σ bond strength for di- σ bonded cyclohexene (205 kJ/mol, see above) and the average C–Pt π bond strength reported for benzene and naphthalene adsorbed on Pt(111) (33 kJ/mol per C atom),^{16,17} the expected σ/π bond strength is

calculated to be $205 + 2 \cdot 33 = 271$ kJ/mol, almost exactly the measured value.

It is also possible to calculate the total bond strength for the π -allyl assuming tri- σ bonding instead of σ/π bonding (see the π -allyl cycle (tri- σ) in Figure 11). This yields a total bond strength of 615 kJ/mol or an average C–Pt σ bond strength of 205 kJ/mol. Interestingly, this is identical to the average C–Pt σ bond strength found for di- σ bonded cyclohexene (205 kJ/mol). Thus, the measured heats do not allow us to confirm that σ/π bonding dominates over tri- σ bonding for π -allyl-c-C₆H₅ on Pt(111). This is in agreement with DFT calculations by Morin et al.,⁸ who find the difference in adsorption energy between a bridge σ/π species and an hcp tri- σ species to be only 6 kJ/mol, with the tri- σ species being the most stable. However, 6 kJ/mol is within the uncertainty of their calculation.

5. Conclusions

Calorimetric measurements of cyclohexene adsorption on Pt(111) in the temperature range from 100 to 293 K identify the heat of adsorption of both intact, di- σ bonded cyclohexene and the first dehydrogenation product 2-cyclohexenyl. Together with previous calorimetric measurements of benzene adsorption on Pt(111),¹⁶ the heat of adsorption of several key intermediates for the dehydrogenation of cyclohexene into benzene have now been identified, a valuable tool for future studies of the catalytic dehydrogenation of cyclohexene.

At 100 K cyclohexene adsorbs on Pt(111) forming intact, di- σ bonded cyclohexene, with an initial heat of adsorption of 130 kJ/mol, giving a standard enthalpy of formation of intact, di- σ bonded cyclohexene on Pt(111) of -135 kJ/mol and an average C–Pt σ bond strength of 205 kJ/mol. This average C–Pt σ bond strength is weaker than those found by King's group for ethylene adsorption on low index platinum surfaces (235–253 kJ/mol).^{47,48} A possible explanation for this is the large amount of strain in the di- σ bonded cyclohexene molecule.³⁴ The coverage-dependent heat of adsorption of di- σ bonded cyclohexene is well described by a second-order polynomial ($130 - 47\theta - 1250\theta^2$) kJ/mol. At 100 K the multilayer adsorption energy for cyclohexene is 47 kJ/mol, in good agreement with previous values of 44 kJ/mol (see above) and 42 kJ/mol.²⁴ At 281 K cyclohexene dehydrogenates on Pt(111), forming adsorbed hydrogen and 2-cyclohexenyl (c-C₆H₅), with an initial heat of adsorption of 174 kJ/mol, giving a standard enthalpy of formation of adsorbed 2-cyclohexenyl on Pt(111) of -143 kJ/mol. The coverage-dependent heat of adsorption of cyclohexene forming adsorbed 2-cyclohexenyl is well described by a second-order polynomial ($174 - 700\theta + 761\theta^2$) kJ/mol. The agreement between our measured heats of adsorption and recent DFT calculations by Morin et al.⁸ is excellent (within 10 kJ/mol) for both di- σ bonded cyclohexene and 2-cyclohexenyl.

At coverages below 0.10 ML, the sticking probability of cyclohexene on Pt(111) is close to unity (>0.95) throughout the temperature range studied (100–300 K), indicating a precursor mediated adsorption mechanism. A similar behavior has been observed for benzene and naphthalene adsorption on Pt(111).^{16,17} During multilayer formation at 100 K, the sticking probability of cyclohexene is 1.00.

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