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Thermochemistry of the selective dehydrogenation of cyclohexane to benzene on Pt surfaces

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Abstract

We use a quasiempirical valence bond (QVB) scheme [E.A. Carter, Chem. Phys. Lett. 169 (1990) 218] for calculating the heats of formation of adsorbed species on surfaces to provide reliable estimates of the relative stabilities of several of the surface intermediates and adsorbate-surface bond strengths that are important in the selective dehydrogenation of cyclohexane to benzene over Pt surfaces. We estimate heats of adsorption and formation for adsorbed cyclohexyl (c-C_6H_{11}), a cycloallylic intermediate (c-C_6H_9), cyclohexadiene (c-C_6H_8), cyclohexadienyl (c-C_6H_7), phenyl (c-C_6H_5), and benzyne (c-C_6H_4) on Pt surfaces. Estimates of these needed formation energies are then combined with the experimentally measured adsorption energies of cyclohexane (c-C_6H_{12}), cyclohexene (c-C_6H_{10}), and benzene (C_6H_6), to provide heats of reaction and an equilibrium thermodynamic description of a selective dehydrogenation mechanism that involves the step-wise, sequential removal of one H atom at a time from cyclohexane to form benzene. In addition, several further decomposition products of benzene are considered as precursors to undesirable carbon-forming reactions. In agreement with experimental observations, a cycloallylic species (c-C_6H_9) is shown to be an important stable intermediate in cyclohexane dehydrogenation that could also be involved in the catalytic rate-limiting step. Carbon–carbon bond cleavage and other possible surface reaction pathways are not considered herein. Addition of measured or estimated values for the activation barriers involved in the reaction on Pt(111) can now give a fairly complete description of the energetics of this prototypical hydrocarbon conversion reaction on Pt(111) surfaces. © 1998 Elsevier Science B.V.

Keywords: Cyclohexane; Benzene; Pt

1. Introduction

The dehydrogenation of cyclohexane to benzene is a prototypical hydrocarbon reforming reaction [1,2] that has been studied extensively at the molecular level in ultrahigh vacuum (UHV). On Pt(111), which is the substrate most thoroughly investigated, some of the intermediates, i.e., cyclohexene and a C_6H_9 species, have been identified and the rate constants for some of the sequential reaction steps have been measured [3–5]. Dehydrogenation of cyclohexane to benzene proceeds efficiently on Pt(111), but very little benzene is desorbed into the gas phase since the Pt surface readily dehydrogenates the benzene product. Studies of the cyclohexene intermediate have been carried out. Also, studies are available for cyclohexyl and

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cyclohexadiene, which are likely intermediates in the reaction. In related work, the influence of Bi [6] and Cs [7] adatoms on this reaction, as well as many aspects of this reaction on ordered Pt–Sn alloys [8–10] have also been investigated.

Even with all of the experimental work, several of the likely intermediates associated with this reaction are still unidentified. The primary challenge is to observe and identify metastable intermediates by surface spectroscopic methods and this is an elusive goal. Another key goal is to determine the adsorption bond strengths and surface bond energies for the reactant, products, and intermediates in the reaction in order to provide a thermochemical description of the reaction. Temperature programmed desorption (TPD) and laser induced thermal desorption (LITD) have been used for estimating the adsorption energies of cyclohexane, cyclohexene, and benzene. Unfortunately, these methods cannot be used for several of the adsorbed hydrocarbon intermediates, since the barriers to subsequent surface reactions are less than the corresponding desorption activation energies and thus decomposition reactions occur rather than desorption into the gas phase. Furthermore, adsorbed molecules of this size are beyond the scope of current first principles theoretical methods. Yet, it is essential to obtain equilibrium thermodynamic data on the relative stabilities of surface species in order to better understand the mechanism of this reaction. In this paper, we utilize a scheme that can be used to estimate the stabilities of surface species in order to provide an energetic foundation for the mechanism of selective dehydrogenation of cyclohexane to benzene. Below, we briefly summarize the experimental observations for this reaction and various mechanisms that have been postulated to explain the experimental data.

The adsorption and decomposition of cyclohexane on the Pt(111) surface have been studied using a variety of surface science methods [3–8,11–24]. Cyclohexane adsorbs molecularly at 100 K. Vibrational studies with both high resolution electron energy loss spectroscopy (HREELS) [13,23] and reflection-absorption IR spectroscopy (RAIRS) [20] have shown that cyclohexane is adsorbed with the molecular plane parallel to the surface with C_{3v} symmetry, probably in a chair configuration with three axial H atoms projecting toward the surface, forming hydrogen bonds. Adsorption leads to a broad, low frequency C–H stretching band due to extensive ‘softening’ of the axial C–H bonds. The surface coverage in the monolayer is between 0.13 [8] to 0.21 [6] monolayer (ML). Upon heating, some cyclohexane desorbs, but most of it (68% [6]) converts to adsorbed benzene which decomposes to hydrogen and adsorbed carbon. Under UHV conditions, no significant gas-phase benzene is produced following cyclohexane adsorption. From the fraction of cyclohexane desorbed in TPD at 228 K, an adsorption energy of 13.9 kcal/mol can be estimated [8]. Dehydrogenation begins at 180–195 K, corresponding to an activation energy, E_a, of 9.5–13.5 kcal/mol over the 5–30% ML coverage range [5]. Benzene is not formed until 300 K [3–5,23], in contrast to early reports of benzene formation at 200 K [6,18]. Unfortunately, cyclohexene (c-C_6H_{10}) remains as the only species from cyclohexane dehydrogenation that has been identified on Pt(111) [3], although an intermediate with C_6H_9 stoichiometry has been inferred to exist over the temperature range 180–270 K using LITD combined with Fourier transform mass spectroscopy (FTMS) [4] and bismuth-postdosing thermal desorption spectroscopy (BPTDS) [22], with the form of this species favored to be a cycloallylic (c-C_6H_9) structure, rather than a simple loss of three axial hydrogens, as deduced from HREELS data [23]. No direct evidence exists for cyclohexyl (c-C_6H_{11}), cyclohexadiene (c-C_6H_8), or cyclohexadienyl (c-C_6H_7) formation from cyclohexane.

Some information has recently become available for the reactivity of the chemisorbed cyclohexyl species on Pt(111). Using electron induced dissociation (EID), low energy electron bombardment of physisorbed layers of cyclohexane was used to cleanly prepare monolayer coverages of adsorbed cyclohexyl species [8,25]. In TPD experiments, H_2 was the dominant reaction product desorbed, with no cyclohexene and only small amounts of benzene desorption observed. The H_2 evolution in the TPD spectra was H_2 desorption rate-limited, and so no information is available on the activation energy for subsequent C–H bond breaking in adsorbed cyclohexyl. However, on two ordered Sn/Pt(111) surface alloys which are less reactive than Pt(111), cyclohexene desorption is observed in two peaks at 208 and 345 K. The peak at 208 K is cyclohexene desorption rate-limited with a desorption energy of 12.6 kcal/mol, and so we can place an upper limit on the activation barrier for the reaction of cyclohexyl on Pt(111) to be 12.6 kcal/mol.

Cyclohexene adsorption on Pt(111) has been investigated by several groups [3,4,6,9,11,15, 22,24]. Generally, it is thought that cyclohexene adsorbs molecularly on the Pt(111) surface at 100 K. TPD and HREELS show two different states of molecularly adsorbed cyclohexene in the first adsorbed layer. The desorption energy of the most tightly bound state desorbing at 281 K in TPD (at the same temperature as ethylene) is 17.1 kcal/mol [9]. Both of these states are correlated to di-σ-bonded cyclohexene as revealed by HREELS but in two different conformations. The saturation monolayer coverage is 0.14 [9] to 0.23 [19] ML. Upon heating, cyclohexene begins to dehydrogenate at 150 K at low coverages [4], with $E_a \cong 9$ kcal/mol, or at higher coverages at 200–240 K ($E_a = 14.4$ kcal/mol) [22]. Greater than 75% [9,19] of the chemisorbed layer decomposes during TPD. A C_6H_9 reaction intermediate in this reaction has also been identified. Benzene is formed on the surface at temperatures near 300 K ($E_a \cong 18$ kcal/mol), and Henn et al. [22] deduced that the barrier for conversion of the c-C_6H_9 species to benzene was 20.8 kcal/mol. Further heating causes a fraction of the benzene formed to desorb from the surface at 400–500 K and the remaining benzene to decompose to hydrogen and adsorbed carbon.

The adsorption and reaction of both 1,3-cyclohexadiene and 1,4-cyclohexadiene on Pt(111) have been investigated [4,10,11,15, 24,26]. Cyclohexadiene chemisorption is completely irreversible and upon heating it dehydrogenates to form benzene. Further heating causes this adsorbed benzene product to either desorb from the surface or dehydrogenate completely to form surface carbon. HREELS [26] and SFG [24] indicate that the nature of the surface bonding is a quadra-σ-type with four covalent Pt–C bonds with sp^3 hybridization at those carbons. In the SFG studies, a red-shift of the C–H stretching frequency to 2770 cm^{-1} was observed and interpreted as a strong interaction between the surface and the CH_2 groups [24]. Saturation coverage for chemisorbed cyclohexadiene is about 0.18 ML [10,26]. LITD/FTMS experiments show that the activation energy for conversion of cyclohexadienes to benzene is very low (at low coverages conversion occurs at 115 K, ($E_a \cong 7$ kcal/mol)) [4], but studies using BPTDS indicate that dehydrogenation of both 1,3- and 1,4-cyclohexadiene occurs at 230–260 K with an activation energy of 14 ± 2 kcal/mol [26].

The adsorption and reaction of the product of this reaction, benzene, has been extensively studied on Pt(111) [6,8,16,17,27–32]. Benzene adsorbs molecularly on Pt(111) at low temperatures with the ring plane parallel to the surface [16,17,27,29,30]. The monolayer coverage is about 0.16 ML [8,32]. No desorption of benzene occurs at low coverages, but a state is formed at higher coverages that desorbs at 480 K. With increasing coverage in the chemisorbed monolayer, this peak grows and shifts to 450 K and a new broad peak forms at 320 K [8]. Desorption activation energies of 30 and 20 kcal/mol can been estimated for the high and low temperature desorption states, respectively. About 55% of the benzene monolayer dehydrogenates upon heating [32], and reaction rate-limited H_2 evolution in peaks at 400, 500, and 525–750 K in

TPD gives the barriers for benzene decomposition to be 24.7 and 31.1 kcal/mol for losing one H and three H atoms, respectively [8].

While it seems clear that cyclohexene (c-C_6H_{10}) and a cycloallylic species (c-C_6H_9) are isolable, stable intermediates in cyclohexane decomposition, and cyclohexyl (c-C_6H_{11}) and cyclohexadiene (c-C_6H_8) are highly likely intermediates due to the benzene formation in their dehydrogenation reactions, there is little direct experimental information available concerning the mechanism of conversion of cyclohexane to benzene on Pt(111). However, most investigators would likely consider a sequential, dehydrogenation mechanism as follows. Cyclohexane adsorbs and dissociates to form cyclohexyl (c-C_6H_{11}). Step-wise loss of H atoms leads to cyclohexene (c-C_6H_{10}), a cycloallylic species (c-C_6H_9), cyclohexadiene (c-C_6H_8), cyclohexadienyl (c-C_6H_7) and then to benzene (C_6H_6) on Pt surfaces. Benzene desorption is then required to form the gas phase product of the selective dehydrogenation reaction.

Previous theoretical work assessing mechanistic aspects of cyclohexane decomposition on Pt has been limited to semiempirical methods. The calculations of Kang and Anderson [33] were carried out using the semiempirical Atom Superposition-Electron Delocalization Molecular Orbital (ASED-MO) method for the binding of various C_6 hydrocarbons on clusters of 15 Pt atoms. A point to be kept in mind is that since this method is not a total energy method and is in addition only a rough approximation to Hartree–Fock theory (which itself is not able to describe covalent metal–carbon bonds properly [34]), it cannot be expected to provide reliable relative energetics. With this caveat, we summarize their findings. In their model, cyclohexane is adsorbed with a binding energy of 8.5 kcal/mol. The barrier for C–H bond cleavage in cyclohexane is calculated to be 29.5 kcal/mol, and the activation barriers for a second and third hydrogen transfer from the lower axial C–H bonds are calculated to be 27.4 and 17.5 kcal/mol. The c-C_6H_9 intermediate thus formed is strongly bound to the surface by 89.7 kcal/mol and is calculated to have a relatively low barrier to 10.1 kcal/mol for the first subsequent C–H bond cleavage. Kang and Anderson conclude that the other two hydrogens come off with lower barriers to form benzene and did not calculate aspects of this last step. In summary, they find that the initial removal of a H atom from cyclohexane is the slowest step in the dehydrogenation mechanism, followed by the formation of the c-C_6H_9 intermediate which loses three more H atoms even more easily. This is in contrast to the experimental observation of the c-C_6H_9 intermediate's respectable stability.

Some time ago, we presented a quasiempirical valence bond (QVB) scheme for calculating the heats of formation of adsorbed species on surfaces [35,36]. This approach is a powerful method for roughly estimating the relative stabilities of surface intermediates and adsorbate-surface bond strengths. The first application of this method considered the mechanism and energetics of ethylene decomposition on Pt(111) [36]. In this study we estimated the heats of formation, heats of reaction, and Pt–carbon bond strengths for adsorbed ethylene, ethylidene, ethylidyne, ethyl, vinyl, acetylene, vinylidene, ethynyl, methyl, methylene, methyne and carbide. While the details of the mechanism of ethylene to ethylidyne conversion continues to be debated and investigated, it is important to point out the strong support for the validity of our method that has been accumulating recently. First, our method relies on an accurate knowledge of the Pt–C bond strength. Our previous work used $D(\text{Pt–C}) = 53$ kcal/mol, which was based on an ab initio value from a Pt–CH_3 complex [37,38]. Single crystal microcalorimetry measurements recently made in King's lab [39] to directly measure the adsorption energies of di-σ-bonded ethylene at low temperatures and ethylidyne (from ethylene adsorption) at 300 K can be used [40] to provide another estimate of the Pt–C bond strength of 57.6 kcal/mol, in fairly good agreement with our previous estimate. Second, in agreement with our equilibrium thermodynamic predictions for the most stable C_2 hydrocarbon surface species [36], ethylidene was identified using NMR over Pt catalysts at high pressures [41]. Also, work from Somorjai's lab [42] using SFG to study the dehydrogenation of ethylene assigned the intermediate detected to ethylidene, in agreement with our suggested decomposition mechanism.

The success of our method for illuminating important aspects of the mechanism of ethylene decomposition prompted the present study. In the next section, we outline and illustrate our strategy for calculating equilibrium thermodynamic energetics of the adsorbates and reactions necessary to describe selective cyclohexane dehydrogenation to benzene on Pt surfaces. The mechanism of benzene decomposition is also interesting and very important to understand for eliminating undesirable coking products, however we will not consider these issues in the present context except for the likely initial steps involving the formation of phenyl and benzyne.

2. Results and discussion

2.1. Scheme for calculating heats of formation of adsorbates on surfaces

In order to calculate heats of formation of c-C_6 adsorbates of interest for cyclohexane dehydrogenation, the heats of formation of the corresponding gas phase species and the surface-adsorbate bond energies must both be known. In general, these adsorbates correspond to gas phase molecular fragments that are relatively unstable (i.e., radicals or excited states) and hence their heats of formation are not directly measurable. Furthermore, most surface-adsorbate bond energies for such fragments are also unavailable. We have developed a general approach for estimating heats of formation for adsorbates [35], involving a straightforward, simple procedure: (i) determine how many chemical bonds are formed from the adsorbate to the surface and characterize them according to either primarily covalent, ionic, or donor–acceptor character; (ii) obtain the experimental heat of formation for the gaseous species in its ground electronic state (or estimate it via a Born–Haber cycle of known heats of formation and bond dissociation energies); (iii) use electronic excitation energies, electron affinities, or ionization potentials to calculate a heat of formation for a gas phase species that most resembles the local electronic state of the molecule when it is adsorbed on the surface; and finally (iv) use measured heats of adsorption (where available) or use estimated or calculated bond energies (from, for example, ab initio electronic structure calculations) for σ and π covalent or donor–acceptor bonds [43,44] to predict the heat of formation of the adsorbed species by subtracting the adsorbate-surface bond energies from the gas phase heats of formation discussed in (iii). Table 1 provides schematic drawings and heats of formation for several c-C_6 gas

Table 1
Structures and heats of formation, $\Delta H^\circ_{f,300}$ (kcal/mol), for the electronic ground states of gas phase c-C_6 species used to calculate the energies of c-C_6 adsorbates

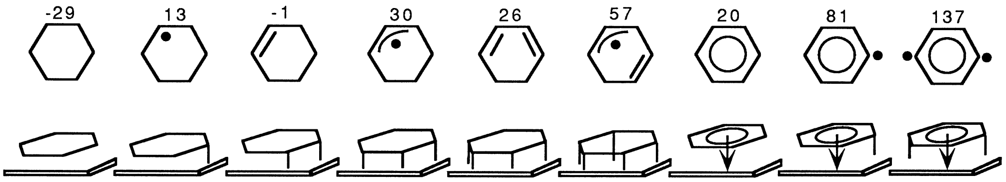

Table 2
Estimated heats of formation ($\Delta H^{\circ}_{f,300}$) for C_6 adsorbates on Pt(111) and related gas phase values

Species	$\Delta H^{\circ}_{f,300}$	References
$C_6H_{12(g)}$ cyclohexane	−29	[45]
$C_6H_{12(a)}$	−43	[8]
c-$C_6H_{11(g)}$ cyclohexyl radical	13	[45]
c-C_6H_{11}—$_{(a)}$	−40	
$C_6H_{10(g)}$ cyclohexene	−1	[45]
$C_6H_{10(g)}$ (∗)	88	
$C_6H_{10(a)}$ di-σ-bonded	−18	[9]
c-$C_6H_{9(g)}$ cycloallylic radical	30	[45]
c-$C_6H_{9(g)}$ (∗)	119	
c-$C_6H_{9(a)}$ tri-σ-bonded	−40	
$C_6H_{8(g)}$ 1,3-cyclohexadiene	26	[45]
$C_6H_{8(g)}$ (∗)	204	
$C_6H_{8(a)}$ tetra-σ-bonded	−8	
$C_6H_{8(g)}$ 1,4-cyclohexadiene	26	[45]
$C_6H_{8(g)}$ (∗)	204	
$C_6H_{8(a)}$ tetra-σ-bonded	−8	
c-$C_6H_{7(g)}$ cyclohexadienyl	57	[45]
c-$C_6H_{7(g)}$ (∗)	235	
c-$C_6H_{7(a)}$ penta-σ-bonded	−30	
$C_6H_{6(g)}$ benzene	20	[45]
$C_6H_{6(a)}$	−10	[8]
c-$C_6H_{5(g)}$ phenyl radical	81	[46]
c-$C_6H_{5(a)}$ σ-bonded	28	
c-$C_6H_{5(a)}$ σ + π-bonded	−2	
o,m,p-$C_6H_{4(g)}$ (singlet) benzyne	107,122,137	[47]
o,m,p-$C_6H_{4(g)}$ (triplet)	145,139,139	[48,49]
o,m,p-$C_6H_{4(a)}$ di-σ-bonded	39,33,33	
o,m,p-$C_6H_{4(a)}$ di-σ + π-bonded	9,3,3	
$H\cdot_{(g)}$ (^2S)	52	[45]
H—$_{(a)}$	−10	[50]

phase molecules in their electronic ground states, as required in step (ii), and also gives (highly) schematic drawings of adsorbed species on Pt(111) that show the correlation between the gaseous and adsorbed species and indicate the bonding to the surface, as required for steps (iii) and (iv). The heats of formation for both gas phase and adsorbed species on Pt(111) are summarized in Table 2.

The heats of formation of the gas phase species were obtained as follows. Values of $\Delta H^{\circ}_{f,300}$ for c-C_6H_x, $x = 6$–12, and H atom were taken directly or derived from Benson's compilation [45]. Values for phenyl radical (c-C_6H_5), and *ortho*-, *meta*-, and *para*-benzyne (c-C_6H_4) were taken from more recent data [46]. The method for obtaining heats of formation of the adsorbed species requires knowledge of the Pt–C σ-bond energy and (possibly) singlet–triplet excitation energies to 'prepare' π-bonds to form di-σ-bonds to the surface. In previous work [36], we employed $D(\text{Pt–C}) = 53$ kcal/mol, an ab initio value for Pt–CH_3 complexes [37,38]. We will also employ 53 kcal/mol throughout this paper as our Pt–C single bond energy. This value is supported by measurements of the activation energy for conversion of cyclohexyl to cyclohexene on Sn/Pt(111) alloys that place this E_a at about 13 kcal/mol [9]. Given that Pt(111) is a more reactive surface than these alloys, we view this value as an upper bound for Pt(111) surfaces. This then provides an upper bound for the Pt–C single bond strength, which is obtained from the inequality requiring the endothermicity to be less than or equal to the activation barrier of 13 kcal/mol:

$$\left\{\Delta H^{\circ}_{f,300}(\text{c-}C_6H_{10(a)}) + \Delta H^{\circ}_{f,300}(H_{(a)})\right\} - \Delta H^{\circ}_{f,300}(\text{c-}C_6H_{11(a)}) \le 13.$$

Now, using $\Delta H_{ads}(\text{c-}C_6H_{10(g)}) = 17$ kcal/mol [9] and $\Delta H^{diss}_{ads}(H_{2(g)}) = 19$ kcal/mol [50], then we have the following relations:

$$\Delta H^{\circ}_{f,300}(c\text{-}C_6H_{10(a)}) = \Delta H^{\circ}_{f,300}(c\text{-}C_6H_{10(g)}) - \Delta H_{ads}(c\text{-}C_6H_{10(g)}) = -1 - 17 = -18\,\text{kcal/mol}$$

$$\Delta H^{\circ}_{f,300}(H_{(a)}) = \Delta H^{\circ}_{f,300}(H_{(g)}) - \Delta H_{ads}(H_{(g)}) = 52.1 - 62 = -10\,\text{kcal/mol},$$

where

$$\Delta H_{ads}(H_{(g)}) = \left[D(H - H_{(g)}) + \Delta H^{diss}_{ads}(H_{2(g)})\right]/2,$$

and

$$\Delta H^{\circ}_{f,300}(\text{c-}C_6H_{11(a)}) = \Delta H^{\circ}_{f,300}(\text{c-}C_6H_{11(g)}) - D(\text{Pt–C}) = 13\,\text{kcal/mol} - D(\text{Pt–C}).$$

And so, using only experimentally measured heats of adsorption and activation barriers, along with well-known gaseous heats of formation in the above equations (vide infra), we obtain

$$-18 - 10 - \{13 - D(\text{Pt–C})\} \leq 13\,\text{kcal/mol}$$

and therefore $D(\text{Pt–C}) \leq 54$ kcal/mol. Thus, the experimental bound on the activation energy for dehydrogenation of adsorbed cyclohexyl provides us with an upper bound of 54 kcal/mol on the Pt–C single bond strength, in excellent agreement with our chosen ab initio value of 53 kcal/mol. Furthermore, the microcalorimetry-derived value of 57.6 kcal/mol [40] mentioned previously is within 5 kcal/mol of the value that we are using (an increase of 4 kcal/mol for the adsorption energy of cyclohexene at zero coverage is required for this value to be consistent with the above arguments as well).

Once this value is fixed, we can now derive, based on the heat of adsorption of cyclohexene, the appropriate singlet–triplet excitation energy (ΔE_{ST}) to employ in order to prepare C–C π-bonds to form di-σ-bonds to the metal. Again, the method prescribes starting with the gaseous species in its ground state (here cyclohexene), exciting up to a ‘bond-prepared’ state (via, e.g., a singlet-to-triplet excitation), and then forming the appropriate number of metal–carbon bonds to obtain heats of adsorption/formation. Since we know $\Delta H^{\circ}_{\text{f},300}$ (cyclohexene$_{(\text{g})}$) = −1 kcal/mol and we know its $\Delta H_{\text{ads}} = -17$ kcal/mol, using $D(\text{Pt–C}) = 53$ kcal/mol one can derive $\Delta E_{\text{ST}} = 89$ kcal/mol for the appropriate singlet–triplet splitting to bond-prepare a cyclic π bond. This is exactly the same value as calculated previously for ethylene (Ref. [36] and E.A. Carter, unpublished). We will use $\Delta E_{\text{ST}} = 89$ kcal/mol per π bond to estimate the energies of all high spin radicals that are required. For example, in the case of cyclohexadiene, we will estimate that the high spin excited state is $2 \times 89 = 178$ kcal/mol above the ground state, since two π bonds are being excited (it is bound to be at least this high, based on Pauli repulsion arguments, and recent ab initio calculations [51] place this planar quintet state in butadiene at $\cong 185$ kcal/mol, consistent with our estimate). This is how $\Delta H^{\circ}_{\text{f},300}$ for the high spin excited state radicals C_6H_x*, $x = 7$–10, shown in Table 2, were calculated.

Finally, values for $\Delta H^{\circ}_{\text{f},300}$ of gaseous, triplet benzynes were calculated as follows. The experimental values of $\Delta H^{\circ}_{\text{f},300}$ of the ground singlet states were added to appropriate single–triplet splittings. Only the ΔE_{ST} for *ortho*-benzyne has been measured [48]. However, correlation-consistent multireference CI calculations [52] have predicted all three, and the error in the calculation compared to the *ortho*-benzyne experimental result is only 2 out of 38 kcal/mol. Thus, we used the other ab initio values of 17 and 2 kcal/mol for ΔE_{ST} for *meta*- and *para*-benzyne, respectively.

The heats of formation of the adsorbates were obtained from the procedure outlined above for estimating these values, except for adsorbed cyclohexane, cyclohexene, and benzene, where the experimental heats of adsorption were used. We consider adsorbed species forming the maximum number of σ-covalent bonds to the surface, with no π-bonding interactions. Since cyclohexene and cyclohexadiene are known experimentally to adopt η^2- and η^4-configurations upon adsorption, we believe this is the preferred geometry for these other species as well. However, reaction energetics involving π-bonding configurations could be easily calculated (if desired) simply by using the corresponding appropriate gas phase heats of formation. We did include π bonding in addition to σ-bonding for phenyl and the benzyne isomers, because of the uncertainty about the nature of the surface bonding and the experimental evidence that phenyl on Cu(111) is inclined only about 30° above the surface plane [53]. We used the π-bond strength of benzene (30 kcal/mol) to the surface as our rough estimate of (and presumably an upper limit to) this stabilization. We include, for completeness, values for phenyl and the benzynes without the π-bonding stabilization, and one sees that this leads to quite a large value (28 kcal/mol) for the endothermicity of the conversion of benzene to phenyl. However, this value is close to a measured barrier of 24.7 kcal/mol for the initial dehydrogenation of benzene [8], and so either this species describes well the chemical nature of phenyl on the surface, with the endothermicity of reaction accounting for the barrier, or it represents an intermediate formed in the conversion of benzene to a more stable adsorbed $\sigma + \pi$-bonded phenyl. Finally, we did not include any estimate of H bonding in species other than cyclohexane, since in general no vibrational signatures of such bonding (i.e., softening of the C–H vibrations) have been observed spectroscopically (there is one unconfirmed report of such interactions for cyclohexadiene [24]).

We derived $\Delta H^\circ_{f,300}$ (values again shown in parentheses) for: (i) adsorbed cyclohexane (-43 kcal/mol) by subtracting the measured heat of adsorption on Pt(111) (13.9 kcal/mol, [8]) from $\Delta H^\circ_{f,300}$(c-$C_6H_{12(g)}$); (ii) adsorbed cyclohexyl, c-C_6H_{11} (-40 kcal/mol) by subtracting the Pt–C single σ bond energy (53 kcal/mol [37,38]) from $\Delta H^\circ_{f,300}$(c-$C_6H_{11(g)}$); (iii) adsorbed cyclohexene (-18 kcal/mol) by subtracting the measured heat of adsorption on Pt(111) (17.1 kcal/mol, [9]) from $\Delta H^\circ_{f,300}$(c-$C_6H_{10(g)}$); (iv) adsorbed c-C_6H_9 (-40 kcal/mol) by subtracting the chemisorption bond energy (159 kcal/mol) from ($\Delta H^\circ_{f,300}$(c-$C_6H_{9(g)}$) + ΔE_{ST} (89 kcal/mol)), assuming that c-C_6H_9 forms three covalent σ bonds to the surface, each worth 53 kcal/mol; (v) adsorbed cyclohexadiene, c-$C_6H_{8(a)}$ (-8 kcal/mol) by subtracting the chemisorption bond energy (212 kcal/mol) from ($\Delta H^\circ_{f,300}$(c-$C_6H_{8(g)}$) + $2\Delta E_{ST}$ (178 kcal/mol)) assuming that c-C_6H_8 forms four covalent σ bonds to the surface, each worth 53 kcal/mol; (vi) adsorbed c-C_6H_7 (-30 kcal/mol) by subtracting the chemisorption bond energy (265 kcal/mol) from ($\Delta H^\circ_{f,300}$(c-$C_6H_{7(g)}$) + $2\Delta E_{ST}$), assuming that c-C_6H_7 forms five covalent σ bonds to the surface, each worth 53 kcal/mol; (vii) adsorbed benzene (-10 kcal/mol) by subtracting the measured heat of adsorption on Pt(111) (30 kcal/mol, [8]) from $\Delta H^\circ_{f,300}$(c-$C_6H_{6(g)}$); (viii) adsorbed hydrogen atom (-10 kcal/mol) by subtracting the experimental Pt–H bond energy (62 kcal/mol, derived from the experimental heat of adsorption (19 kcal/mol) of hydrogen of Pt(111) [50]) from $\Delta H^\circ_{f,300}$($H_{(g)}$); (ix) adsorbed phenyl radical (28 kcal/mol for σ-bonded, -2 kcal/mol for $\sigma + \pi$ bonded) by subtracting the chemisorption σ bond energy of 53 kcal/mol and the chemisorption π bond of 30 kcal/mol from $\Delta H^\circ_{f,300}$(c-$C_6H_{5(g)}$); and (x) adsorbed benzynes (39 and 33 kcal/mol for di-σ only bonding of ortho and meta/para; 9 and 3 kcal/mol for di-$\sigma + \pi$ bonding of ortho and meta/para) by subtracting the σ chemisorption bond energy of 106 kcal/mol and the π chemisorption bond energy of 30 kcal/mol from $\Delta H^\circ_{f,300}$(triplet-benzynes$_{(g)}$).

It is critical to re-emphasize the main assumptions made in calculating these heats of adsorption. First we point out that one must have an understanding of the type and number of adsorbate-surface bonds involved. If one is unsure, the error bars associated with ΔH_{ads} could be large. In the cases presented here, spectroscopic evidence from HREELS established di-σ and quadra-σ bonding for cyclohexene and cyclohexadiene. This suggests we are on firm ground assuming that all unsaturated C atoms in these c-C_6 compounds will form a number of σ-bonds equal to the number of H atoms lost relative to cyclohexane. Benzene is clearly an exception, since the aromaticity of benzene favors π-bonding to the metal. Again, spectroscopic evidence supports π-bonding for benzene and phenyl, while phenyl—having lost an H atom relative to benzene—can use its C radical electron to form an additional σ-bond to the metal.

Secondly, we assume a high spin excited state is required for bonding. Note this is the typical valence bond model of bonding [49] that has been highly successful for gas phase molecules. In addition, confirmation of the quality of our estimate of the energy for such high

Table 3
Estimated heats of elementary reactions of C_6 hydrocarbons on Pt (kcal/mol)

Reaction	Type	ΔH^{rxn}
$C_6H_{12(a)} \rightarrow \eta^1$-c-$C_6H_{11\,(a)} + H_{(a)}$	C–H cleavage	−7
$C_6H_{12(a)} \rightarrow C_6H_{12(g)}$	desorption	14
η^1-c-$C_6H_{11(a)} + H_{(a)} \rightarrow C_6H_{12(a)}$	hydrogenation	7
η^1-c-$C_6H_{11(a)} \rightarrow \eta^2$-$C_6H_{10(a)} + H_{(a)}$	C–H cleavage	12
η^2-c-$C_6H_{10(a)} + H_{(a)} \rightarrow \eta^1$-c-$C_6H_{11(a)}$	hydrogenation	−12
η^2-c-$C_6H_{10(a)} \rightarrow \eta^3$-$C_6H_{9(a)} + H_{(a)}$	C–H cleavage	−32
$C_6H_{10(a)} \rightarrow C_6H_{10(g)}$	desorption	17
η^3-$C_6H_{9(a)} + H_{(a)} \rightarrow \eta^2$-c-$C_6H_{10(a)}$	hydrogenation	32
η^3-$C_6H_{9(a)} \rightarrow \eta^4$-$C_6H_{8(a)} + H_{(a)}$	C–H cleavage	22
η^4-$C_6H_{8(a)} + H_{(a)} \rightarrow \eta^3$-c-$C_6H_{9(a)}$	hydrogenation	−22
η^4-$C_6H_{8(a)} \rightarrow \eta^5$-$C_6H_{7(a)} + H_{(a)}$	C–H cleavage	−32
$C_6H_{8(a)} \rightarrow C_6H_{8(g)}$	desorption	34
η^5-$C_6H_{7(a)} + H_{(a)} \rightarrow \eta^4$-$C_6H_{8(a)}$	hydrogenation	32
η^5-$C_6H_{7(a)} \rightarrow C_6H_{6(a)} + H_{(a)}$	C–H cleavage	10
$C_6H_{6(a)} + H_{(a)} \rightarrow \eta^5$-$C_6H_{7(a)}$	hydrogenation	−10
$C_6H_{6(a)} \rightarrow \eta^6$-$C_6H_{5(a)} + H_{(a)}$	C–H cleavage	−2
$C_6H_{6(a)} \rightarrow C_6H_{6(g)}$	desorption	30
η^6-$C_6H_{5(a)} + H_{(a)} \rightarrow C_6H_{6(a)}$	hydrogenation	2
η^6-$C_6H_{5(a)} \rightarrow \eta^6$-$C_6H_{4(a)} + H_{(a)}$	C–H cleavage	1 (for *o*-); −5 (for *m* or *p*-)

spin states comes from very recent first principles density functional theory calculations on butadiene by Petterson et al. [51] whose predictions for the singlet–quintet splitting in planar butadiene (185 kcal/mol) is roughly twice the vertical singlet–triplet splitting in ethylene (89 kcal/mol), which is the value we proposed to use. We therefore believe that such an estimate of the excited states' energy is valid. One could imagine refining the model by noting that the difference in energy between the first principles excitation energy and our 'additive' excitation energy is 'excess' Pauli repulsion energy due to four spins being in contact rather than two separated groups of two spins. Thus 185-2(89) = 7 kcal/mol might be considered an estimate of this additional repulsion not accounted for in our purely additive model. We retained the purely additive model here for simplicity.

Lastly, the model does not account for lateral interactions between adsorbates and therefore is only applicable to low coverage regimes. This means that when we look at coverage-dependent binding energies and activation barriers, we must be careful to compare only to low coverage values. For endothermic surface reactions, their activation barriers provide upper bounds to the endothermicities and thus allow us to check the consistency of our model. In all cases considered herein and in our past work, this has proven to be true (namely, our endothermicities have been nearly met or exceeded by the corresponding, measured activation barriers).

With our assumptions now clearly defined, we then use these calculated heats of formation for adsorbed species to calculate several heats of reactions of adsorbed hydrocarbons on Pt(111) (Table 3). In Section 2.2, we employ these heats of formation and heats of reaction, along with experimental activation barriers, to obtain a rough potential energy surface for the selective dehydrogenation of cyclohexane to benzene (and beyond) on clean Pt(111).

2.2. Calculated energetics for the dehydrogenation of cyclohexane to benzene on Pt(111)

Fig. 1 displays a mechanism for the reaction of cyclohexane on Pt(111) using the energetics derived above for the step-wise, sequential removal of H atoms from cyclohexane. The energy zero is the heat of formation of the ele-

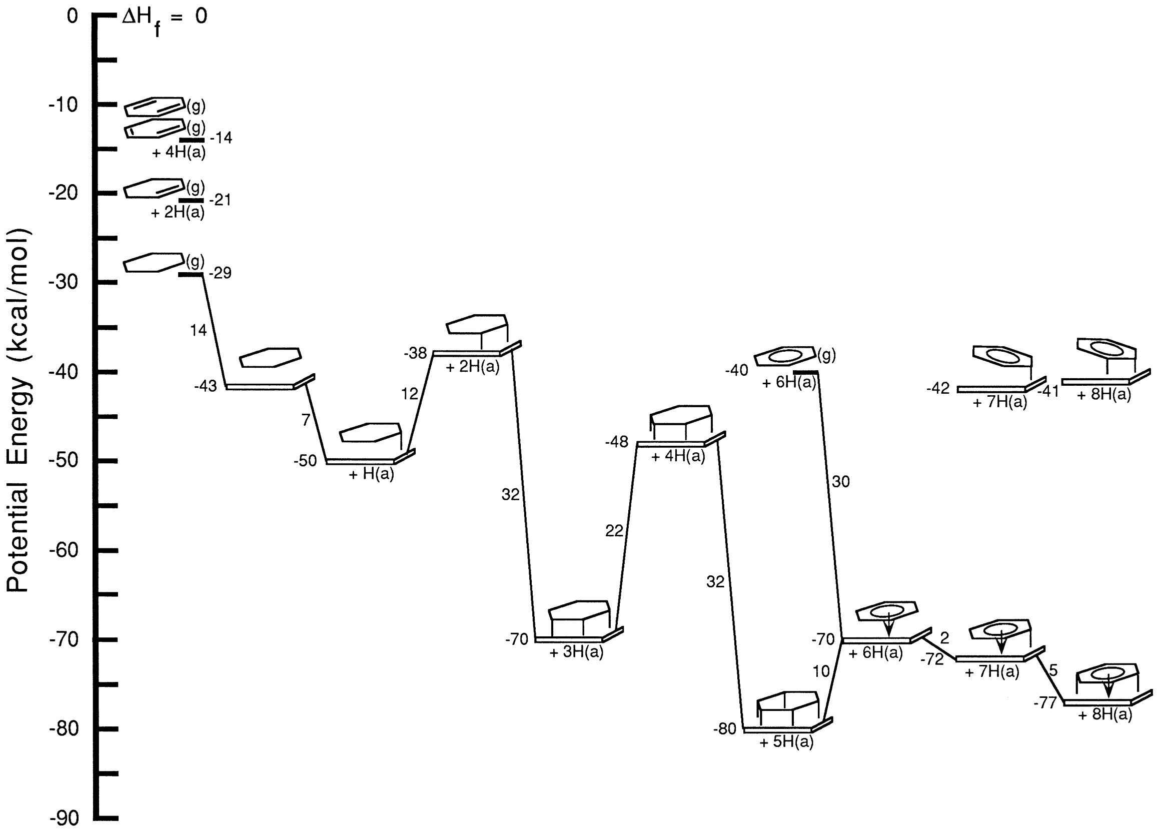

Fig. 1. Thermochemistry for a step-wise, sequential mechanism for dehydrogenation of cyclohexane to benzene on Pt.

ments in their standard states, i.e., $\Delta H^{\circ}_{f,300}(H_{2(g)}) = \Delta H^{\circ}_{f,300}(Pt_{(s)}) = \Delta H^{\circ}_{f,300}(C_{(graphite)}) = 0$. Mass balance requires that we consider the heat of formation of the coadsorbed H atoms required by stoichiometry. This mass balance is required even if the reaction is carried out in vacuum under conditions where the hydrogen recombines and desorbs at equilibrium, since we assume that the nascent products of the reaction include coadsorbed hydrogen, rather than $H_{2(g)}$.

We believe that this diagram does not dramatically change upon changing the Pt crystal face, and so these energetics have some generality for all reactions on Pt, i.e., the Pt–C σ bond strengths are not a strong function of the surface structure. For example, it is well known that *D*(Pt–H) is a constant for Pt(111), (110), and (100). The shortcoming of such a diagram is, of course, the limitations of calculating coadsorption effects on adsorbate bonding due to high coverages of reactants, products, or intermediates.

The appreciable structure-dependent differences in hydrocarbon chemistry on Pt comes principally from structure-dependent changes in activation barriers for reactions, and rather small barrier changes can cause large alterations in the branching ratios among the many reaction paths available for hydrocarbon conversion reactions. Thus, while the thermochemistry contained in Table 3 determines the reaction energetics and the concentrations of these species at equilibrium, the concentrations of these species measured in experiments are often determined by the kinetics of the reactions rather than the thermodynamics. Thus, activation energy barriers for these reactions need to be considered to

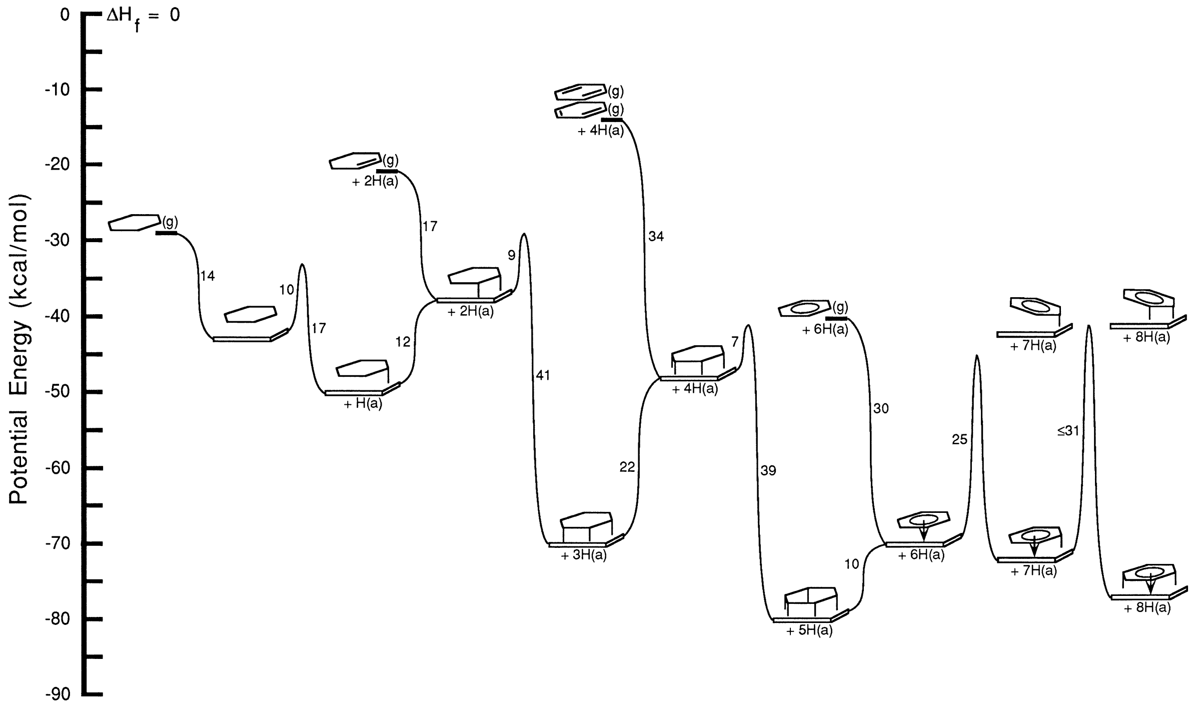

Fig. 2. Reaction energetics for a step-wise, sequential mechanism for dehydrogenation of cyclohexane to benzene on Pt(111).

understand the species formed, and an overall understanding of the reaction energetics requires inclusion of the various activation barriers in the reaction mechanism. The activation energy barriers shown in Fig. 2 are specific to reactions on Pt(111), and were either taken directly from experimental observations on Pt(111) or were deduced from a combination of the experimental activation energies and our calculated thermochemistry. In extracting predictions of unknown barriers, we used these two kinetic principles: (i) if the first elementary step is rate-limiting, then every subsequent barrier en route to a stable intermediate must be lower than the first barrier and (ii) if a later elementary step is rate-limiting, then the barriers for all previous steps en route to a stable intermediate (or final product) must be lower than the observed activation barrier, E_a^{obs}. Below we discuss the heats of and barriers to reaction for various steps in the dehydrogenation of cyclohexane, comparing our predictions to experiment and to previously postulated mechanisms where possible.

Consider first the two possible reaction pathways for cyclohexane adsorbed on Pt(111): dehydrogenation and desorption. We find that the most energetically favorable reaction step (see Table 3) is C–H bond cleavage to form an adsorbed cyclohexyl species (7 kcal/mol exothermic) while desorption of molecular cyclohexane is an unfavorable reaction step (endothermic by 14 kcal/mol). Experimentally (on Pt(111) at saturation coverage), ≅ 32% of the adsorbed cyclohexane is observed to desorb molecularly (E_d = 13.9 kcal/mol [8]), and 68% is observed to decompose via some pathway to form cyclohexene (E_a = 9.5–13.5 kcal/mol for 5–30% ML [5]). Thus, the barrier for dissociation from the molecularly adsorbed state is 9.5–13.5 kcal/mol, while the barrier for desorption is 13.9 kcal/mol, and hence adsorbed cyclohexane is more likely to dissociate than to desorb, especially at low coverages.

Large barriers may exist for C–C bond cleavage compared with those for C–H bond cleavage, since C_x, where $x < 6$, adsorbates are not observed until much higher temperatures, if at all. Indeed, one might expect a higher barrier for C–C bond cleavage compared to C–H bond cleavage because of the less favorable geometry that the carbon atoms must adopt in transition states involving C–C bond cleavage compared to those for C–H bond breaking. However, we should note that the identification of various $C_{x<6}$ adsorbates by unambiguously distinguishing these from possible C_6 hydrocarbon species is difficult at best using most surface analytical spectroscopies and perhaps impossible if mixtures of hydrocarbon adsorbates are formed; thus, the validity of this lack of observation is still an open question. However, these pathways are not considered in this diagram since there is no evidence at this time that such pathways involving C–C bond cleavage lead to appreciable benzene production on Pt(111).

Cyclohexyl dehydrogenates at relatively low temperatures ($E_a \leq 12.6$ kcal/mol [8]) on Pt(111). Using the experimental activation energies given above and our calculated heats of reaction, we predict (Fig. 2) that the barrier for formation of adsorbed cyclohexane from coadsorbed cyclohexyl and hydrogen is 17 kcal/mol and that the endothermicity of reaction to form adsorbed cyclohexene is small, only $\cong 12$ kcal/mol. Thus, the barrier to dehydrogenation of cyclohexyl is essentially the endothermicity of reaction. Confirmation of our prediction for the barrier for formation of adsorbed cyclohexane from coadsorbed cyclohexyl and hydrogen comes from TPD experiments showing reaction-rate limited cyclohexane production at 272 K ($E_a \cong 16.6$ kcal/mol) from hydrogenation of cyclohexene.

Consider the three possible reaction pathways for cyclohexene on Pt(111): hydrogenation, dehydrogenation, and desorption. We find that the most energetically favorable reaction step (see Table 2) is dehydrogenation to η^3-$C_6H_{9(a)}$ (exothermic by 32 kcal/mol), followed by hydrogenation to adsorbed cyclohexyl (downhill by 12 kcal/mol), while desorption of molecular cyclohexene is the least favorable reaction step (endothermic by 17 kcal/mol). Experimentally (on Pt(111) at saturation coverage), $< 25\%$ of the adsorbed cyclohexene is observed to desorb molecularly ($E_d = 17.1$ kcal/mol [9]) and $>$ 75% is observed to decompose ($E_a = 9$–14.4 kcal/mol [4,22]) through a proposed η^3-$C_6H_{9(a)}$ intermediate. The endothermicity we calculate to decompose this intermediate is 22 kcal/mol, and this is consistent with an estimated reaction barrier of 18–20.8 kcal/mol from experimental measurements [4,22]. This reaction forms benzene [4,9,22], presumably through a cyclohexadiene intermediate. It is important to note that the predicted barrier to hydrogenation of cyclohexene to cyclohexyl is nearly zero, and this process is clearly dictated by the concentration of hydrogen on the surface. It might even play a role in the interesting 'two-peak' desorption spectra of cyclohexene [9]. Also, the huge barrier to hydrogenating the η^3-$C_6H_{9(a)}$ intermediate (endothermic by 32 kcal/mol with a barrier predicted to be 41 kcal/mol) eliminates hydrogenation pathways to produce cyclohexane and cyclohexene from any intermediate past c-C_6H_9, including cyclohexadiene and benzene, in agreement with experimental findings.

Consider the three possible reaction pathways for cyclohexadiene on Pt(111): hydrogenation, dehydrogenation, and desorption. We find that the most energetically favorable reaction step (see Table 2) is C–H bond cleavage to form a η^5-$C_6H_{7(a)}$ cyclohexadienyl species (32 kcal/mol exothermic), followed by hydrogenation to adsorbed η^3-c-$C_6H_{9(a)}$ (downhill by 22 kcal/mol), while desorption of molecular cyclohexadiene is the least favorable reaction step (endothermic by 34 kcal/mol). Experimentally, on Pt(111) no adsorbed cyclohexadiene is observed to desorb molecularly, no cyclohexadiene is hydrogenated to cyclohexene, and presumably complete conversion to chemisorbed benzene occurs. This is consistent with Fig. 2. The activation barrier to react η^4-$C_6H_{8(a)}$, presumably to form benzene via a c-$C_6H_{7(a)}$ intermediate, has been measured to be 7–13.5 [4] and 14 ± 2 kcal/mol [26] on Pt(111). The endothermicity we calculate for dehydrogenation of c-$C_6H_{7(a)}$ to benzene is 10 kcal/mol, while that for hydrogenation is 32 kcal/mol. The 10 kcal/mol dehydrogenation endothermicity represents most of the barrier to forming benzene from c-$C_6H_{7(a)}$ since benzene is formed from cyclohexane and cyclohexene at about 300 K [3–5,23], i.e., ($E_a \leq 18$ kcal/mol), and measurements on Pt(111) show benzene desorption at 310 K ($E_a \leq 18.9$ kcal/mol [10]) from cyclohexadiene dehydrogenation. A better (lower) value of the upper limit for this barrier comes from studies on Pt–Sn alloys, where benzene was desorbed in TPD in a peak at 235 K ($E_a = 13.6$ kcal/mol [10]) following cyclohexadiene adsorption on the $\sqrt{3}$-Sn/Pt(111) alloy. This represents an upper limit on the reaction barrier on Pt(111), because this alloy is less reactive than Pt(111), and it is within a few kcal/mol of the value for the calculated endothermicity. Again, we predict little or no barrier for hydrogenation of cyclohexadiene to c-$C_6H_{9(a)}$, and this species should be formed as soon as hydrogen becomes available from dehydrogenation of cyclohexadiene. However, further hydrogenation past c-$C_6H_{9(a)}$ will not occur due to the large barrier (41 kcal/mol) for hydrogenation to cyclohexene.

The final step in the reaction involves the desorption of benzene. It is likely that the more exothermic (and nearly barrierless) hydrogenation reaction does not compete in UHV because of the lack of adsorbed hydrogen under reaction conditions. At temperatures ≥ 300 K, all adsorbed hydrogen immediately desorbs as H_2 so that negligible quantities of $H_{(a)}$ exists at steady-state under ultrahigh vacuum reaction conditions. However, even if hydrogen is available, the conversion of benzene to η^5-$C_6H_{7(a)}$ on clean Pt(111) is a dead end path due to the large barriers encountered for the back (further hydrogenation) reactions.

We also show a likely path for an undesirable reaction, that of benzene decomposition. Our predictions are that the first steps are nearly thermoneutral if phenyl and benzyne are chemisorbed with the ring plane nearly parallel to the surface, with π bonding from the ring contributing strongly to the chemisorption bond, and endothermic by 28–29 kcal/mol for the limiting case of σ-bonded and di-σ-bonded species, respectively, with no π bonding stabilization at all. Importantly, we don't predict huge endothermicities that disagree with the known barriers. Experimentally, on Pt(111) about 55% of the benzene monolayer dehydrogenates upon heating [32] with barriers of 24.7 and 31.1 kcal/mol for losing one H and three H atoms, respectively [8]. Our predicted endothermicities for forming σ-bonded phenyl and di-σ-bonded benzyne without any π bonding stabilization are remarkably close to the activation barriers cited above. Obviously, π bonding contributions to the chemisorption bond will lower the energies of these species. We conclude that either this σ-bonded species describes well the chemical nature of phenyl on the Pt(111) surface, with the endothermicity of this reaction accounting for nearly all of the benzene dehydrogenation barrier, or it represents an intermediate formed in the conversion of benzene to a more stable adsorbed $\sigma + \pi$-bonded phenyl.

An obvious feature of the potential energy diagram of Fig. 1 is that at equilibrium in the presence of hydrogen, adsorbed η^5-C_6H_7 is predicted to be the most stable c-C_6 surface species. An adsorbed η^3-C_6H_9 species is also predicted to be a stable species present in appreciable concentrations due to the relatively large barriers for forward and reverse reactions. This prediction has important implications to hydrocarbon conversion and reforming catalysis where these species should play important roles in the catalytic reaction mechanisms. Figs. 1 and 2 are also consistent with important kinetic and mechanistic aspects of cyclohexane to benzene conversion catalysis at high pressures [1]: (i) kinetics consistent with a simple sequence of irreversible steps; and (ii) the rate determining step being either benzene desorption or the dehydrogenation of some intermediate depending on the reaction conditions. We predict that dehydrogenation of the cycloallylic intermediate is endothermic by 22 kcal/mol and that this is the rate determining step when the kinetics are not rate-limited by benzene desorption.

Two final comments on this energetic and mechanistic analysis can be made. First, new direct measurements of hydrocarbon heats of adsorption or improvements from chemical physics experiments or theoretical calculations of excitation energies for reactive species and of metal–carbon bond strengths will greatly improve our ability to set thermodynamic limits on the stable species formed on surfaces. Secondly, the heats of formation and reaction shown in Tables 2 and 3 and the type of scheme shown in Fig. 1 should be useful in general for understanding the reactions of cyclohexane, cyclohexene, and cyclohexadiene on other metal surfaces, simply by incorporating changes in the calculated heats of adsorption for the hydrocarbon species, as well as any experimental information about the adsorption energies and barrier heights on other surfaces. In particular, the estimates of heats of formation and reaction energetics for the adsorbed hydrocarbon fragments can be obtained by using the appropriate metal–carbon and metal–hydrogen bond energies, dependent on the specific transition metal, since we have already tabulated the heats of formation of the gas phase species in the appropriate electronic state. Thus, this approach and the resulting values for adsorbate heats of formation are expected to lend new insight into the mechanisms of hydrocarbon reactivity on a variety of metal surfaces.

3. Summary

We have applied a quasiempirical valence bond approach for calculating the heats of formation of adsorbed species to understand mechanistic aspects of the selective dehydrogenation of cyclohexane to benzene over Pt(111) surfaces. We have calculated the heats of formation of all the relevant surface species that play a role in sequential dehydrogenation process. These heats of formation were then used to predict the thermochemistry along the pathway to benzene. Barriers to each step were taken from or deduced from experimental data. Throughout our analysis we have made no attempt to include coverage effects on adsorption energies and reaction barriers, in order to simplify the approach. Our calculations indicate that in the sequential dehydrogenation mechanism, a metastable η^3-C_6H_9 allylic intermediate is formed and that the rate limiting step involved in benzene production is either the dehydrogenation of this intermediate to chemisorbed cyclohexadiene or desorption of the benzene product. Finally, we calculate phenyl and benzyne energetics for benzene decomposition reactions that lead to carbon deposition and we find the energetics of those reactions to be consistent with the experimentally measured barriers.

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