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Theoretical Interpretation of the Cyclohexane → Benzene Reaction on the Pt(111) Surface

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Abstract: Cyclohexane is found to bind most strongly to Pt(111) when three axial CH bonds are directly over three surface metal atoms. Bonding to the surface is caused by CH σ donation to the surface which also serves to weaken the CH bonds as noted in the experimental literature. The hydrogen atoms in the axial bonds are easily transferred to surface platinum atoms, with decreasing activation barriers as the C_6H_n intermediate settles closer to the surface as a result of metal-carbon bonding. The barriers to equatorial CH bond scission from C_6H_9 are lower still. The strong CH activation is a consequence of a CH σ donation bond to the surface. Before the transition state is reached during the stretch of a CH bond, the antibonding counterpart orbital to this 3-center C-H-Pt bond donates its electrons to the conduction band. Consequently, the C-H-Pt bond order in the transition state is one. These results explain the experimental observation of benzene formation at low temperature.

In a high resolution electron energy loss spectroscopy (EELS) analysis Demuth et al.[1] observed a softening and broadening of the CH bond stretching vibration frequency upon adsorption of cyclohexane on Pt(111) at $T = 140$ K. They suggested that this shift is associated with an attractive hydrogen bonding interaction between the adsorbate hydrogen atoms and the surface. However, on the basis of recent EELS and TDS (thermal desorption spectroscopy) studies, Hoffmann and Upton[2] have suggested a different origin for CH soft modes in cyclohexane adsorption on isostructural surfaces other than Pt(111). These soft modes were believed not to be dependent on such a H-bonding interaction between the molecule and the surface. An attempt was made to explain the softening in terms of the geometric match between CH bonds of the adsorbate and high-coordinate sites of the substrate. It is of interest to explore theoretically the relationship between mode softening, chemisorption, and CH bond activation. It is important to see if a softening of the CH bond can be closely related to a relatively low barrier to dehydrogenation of cyclohexane to benzene. This activation might be a result of CH σ donation to the surface as discussed in our recent studies of CH bond activation by metals[3-8] and metal oxides.[9]

In this paper, we present the molecular orbital explanation for binding of cyclohexane and hydrogen transfer to the Pt(111) surface. We use a 15-atom cluster model with 12 unpaired electrons in the upper levels of the platinum d band (Figure 1). The method used is the semiempirical atom superposition electron delocalization molecular orbital (ASED-MO) method. parameters for the present study are in Table I. Further detail of this method is given in ref 6 and 7 wherein the results of theoretical studies of the adsorption and reactions of other hydrocarbon molecules on Pt(111) are given.

Results and Discussion

The chair form of cyclohexane is most stable in the gas phase[10] and is used in our adsorption studies. D_{3d} symmetry is taken for the chair conformation. The projection of this form is shown in Figure 2. With use of ref 10, the torsional angles are 56° and the C-C-C angles 111°. The C-C-H and H-C-H angles are 109° and 110°, respectively. These values are used in our theoretical calculations. The axial CH bonds are not perfectly parallel but are oriented outward by about 3°. Because of their importance to our CH activation studies we optimized these angles and also obtained a value of 3°. The C-C bonds are calculated to be 1.74 Å and the C-H bonds 1.19 Å. As in past studies[3-7] the calculations systematically overestimated these bond lengths (by 0.2 and 0.1 Å, respectively) with the present parameters. The above geometry is used in this adsorption study.

Table I. Atomic Orbital Parameters: Ionization Potential (IP) in eV and Slater Orbital Exponents (ζ) in au (from ref 6)

atomic orbital		IP	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Pt	6s	10.00	2.550			
	6p	5.96	2.050			
	5d	10.60	6.013	2.396	0.6562	0.5711
C	2s	19.00	1.658			
	2p	10.26	1.618			
H	1s	12.60	1.200			

[a] Coefficients used in the double-ζ expnasion.

Table II. Binding Energies (BE), Lower Axial CH Bond Stretching Force Constants (k_e), and Heights for Cyclohexane in Various Binding Sites[b]

	site		
	1-fold	2-fold	3-fold
BE (eV)	0.42	0.36	0.34
k_e (mdyne/Å)	4.09	4.49	4.93 (4.65)[a]
H-surface distance (Å)	2.04	2.04	2.04
C-surface distance (Å)	3.23 (3.77)	3.23 (3.77)	3.23 (3.77)

[a] The gas-phase value. [b] Site is for the triangular array of lower axial CH bonds. Distance is defined in Figure 3 showing cyclohexane adsorbed to 2-fold site; values in parentheses in C-surface distance are the second nearest carbon triangular array distances from the surface.

The cyclohexane molecule is taken to be adsorbed with the carbon ring skeleton roughly parallel to the surface so as to maximize the interaction with the surface atoms as shown in Figure 3 for the "2-fold" site, i.e., the site where H atoms are in bridging positions. The lower three axial CH bonds are directed into the surface and the upper three axial CH bonds are directed away from the surface. The remaining six equatorial CH bonds are approximately parallel to the surface. Molecular binding energies are calculated to be in the physisorption range (0.4 eV). In Table II, we show that binding energies are nearly the same on all sites, though the 1-fold site (H atoms directly above metal atoms) is slightly favored and the surface molecule distances are relatively large. The adsorption of cyclohexane on Pt(111) exhibits a very weak molecular adsorbate-substrate interaction. The

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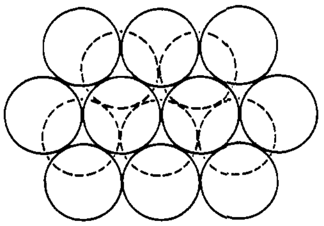

Figure 1. Cluster model of the Pt(111) surface.

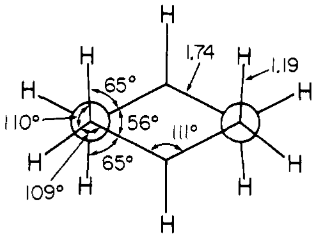

Figure 2. Projection of cyclohexane (gas-phase structure).

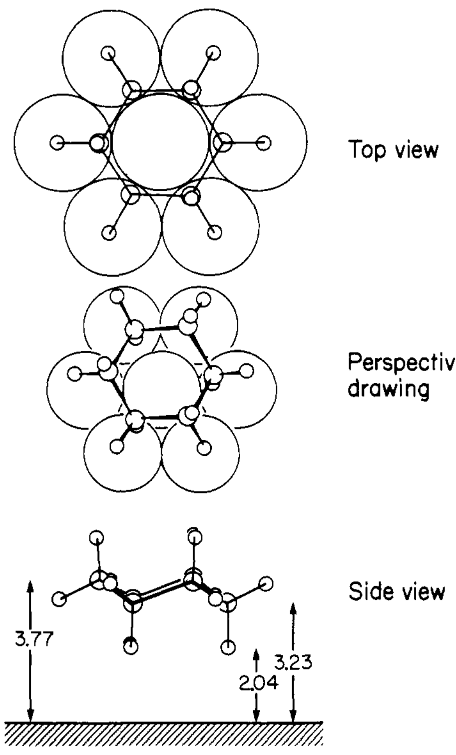

Figure 3. Schematic diagram of the cyclohexane geometry adsorbed to 2-fold site on Pt(111).

geometrical and electronic structures of the gas-phase molecule are only slightly perturbed in the adsorbed layer. As Figure 4 shows, the a_{1g}, e_u, e_g, and a_{2u} symmetry CH σ orbitals are slightly stabilized by σ donation to the surface Pt atoms in the 1-fold site. In the 1-fold and 2-fold sites these CH bonds maintain the predicted gas-phase lengths but in the 3-fold site (H atoms over 3-fold holes) they shrink by 0.01 Å.

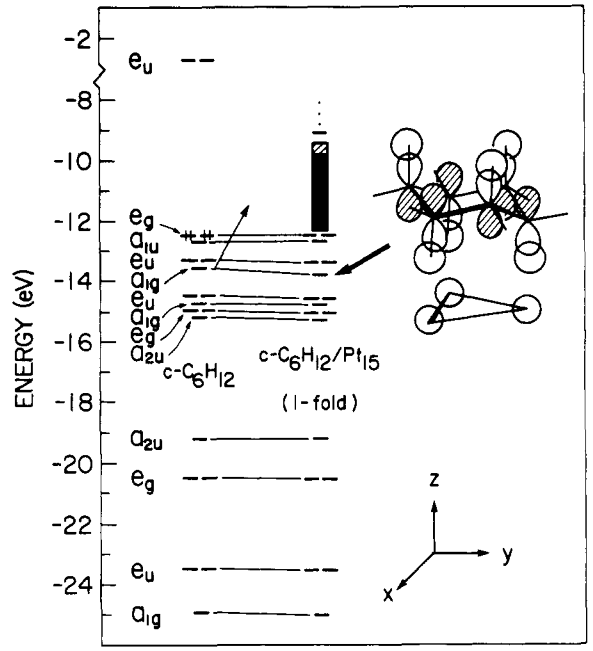

Figure 4. Orbital energy level correlation diagram for cyclohexane adsorbed to the Pt_{15} model of the (111) surface in the 1-fold site. Cross-hatched d band regions are half-filled.

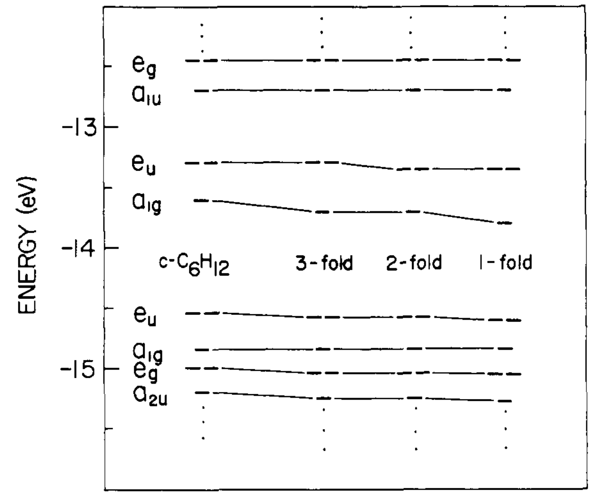

Figure 5. CH σ donation interactions of cyclohexane with various adsorption sites.

A number of recent studies of unsaturated hydrocarbons chemisorbed on transition-metal surface have demonstrated that donation and back-bonding interactions result in a strong chemisorption bond.[3-8] However, the absence of π orbitals in cyclohexane does not allow a strong interaction with the platinum surface. LEED (low energy electron diffraction) analysis by Firment and Somorjai[11] shows ordered monolayer coverages of cyclohexane on Pt(111) at 140–200 K but cyclohexane does not adsorb in an ordered manner above 200 K. The breakdown in ordering is consistent with the weak interaction with the surface. Effectively, the carbon skeleton is held at a relatively great distance from the surface and only three hydrogen atoms of lower axial CH bonds are in contact with it. Bonding interactions of these CH bonds with the surface metal atoms are responsible for the reduced CH stretching frequency in 1-fold and 2-fold sites because of CH σ donation to the surface which delocalizes the bonding electrons.

Demuth et al.[1] have reported that the CH stretching frequency for cyclohexane shifts from the gas-phase value of 2900–3000[12] to 2590 cm^{-1} when cyclohexane is adsorbed on Pt(111) at T = 140 K. The ratio of these frequencies is 0.88 and the ratio of the square roots of the cooresponding force constants in our calculation is 0.94 for the cyclohexane adsorbed on the 1-fold site (Table II). Our theoretical results supports the HREELS observation of a shift due to CH bond weakening on the surface. In contrast, it is found in Table II that the CH force constant in the 3-fold site is slightly larger than the calculated gas-phase value of 4.65 mdyn/Å and in the 2-fold site it is slightly smaller. These results

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are consistent with the reduced σ donation at these sites, as shown in Figure 5.

According to the EELS study of cyclic hydrocarbons adsorbed on Ru(001) at $T = 90$ K by Hoffmann and Upton,[2] the CH mode softening is much more pronounced for C_5 and C_6 molecules when compared to C_3, C_4, and C_8. The exact fitting of CH bonds on the hexagonal surface lattice gives the enhanced lower energy peak intensity because the CH to metal σ donation is maximized when the CH bonds are aimed directly at the surface metal atoms, according to our calculations. Thus the CH soft mode intensity increases with the number of CH bonds pointing vertically at the surface metal atoms. In the C_8 case a weakened CH mode is evident.[2] We find that molecular models indicate the possibility of adsorption with one or at most two CH bonds directed down toward the surface. Possibly this CH bond is weakened.

Hoffmann and Upton[2] have suggested that CH mode softening results from an interaction of lower axial CH bonds with the 3-fold hollow sites rather than 2-fold bridge or 1-fold site because the high-coordinate sites presumably allow the closest approach and thus alignment at those sites should maximize a charge transfer effect because one might expect CH–surface distances to decrease as site coordination increases. As shown in Table II, however, these distances do not change with varying sites, according to our calculations, and CH σ donation favors 1-fold coordination. Hoffmann and Upton found that when the Ru(001) surface was exposed to 1 langmuir of O_2, producing a $^1/_4$ monolayer p(2 × 2) coverage of oxygen atoms located in 3-fold hollow sites, cyclohexane still adsorbed but would not dehydrogenate. Furthermore, no CH frequency shift occurred. This may be a consequence of preference for 3-fold site cyclohexane adsorption in this case. There will be a steric closed shell repulsion between the CH bonding orbitals and the filled O 2p band. Adsorption with the CH bonds in the 3-fold sites will minimize this repulsion. The weakened CH σ donation to the metal surface in this site would account for the absence of mode softening. As will be discussed below, the 3-fold structure is not optimal for CH activation and dehydrogenation to benzene and may be why benzene formation was not observed on the oxidized surface.

Madey and Yates[13] have observed an hexagonal angular distribution of H^+ emitted by electron beam decomposition of cyclohexane on the Ru(001) surface, which is isostructural to Pt(111). They concluded that the chair form cyclohexane molecules are randomly distributed in the two rotational conformations that are possible for 3-fold adsorption. However, 1-fold and 2-fold adsorptions are also consistent with the 6-fold H^+ desorption pattern.

Muetterties et al.[14] have shown that cyclohexane adsorbed on Pt(111) desorbs reversibly with maximum desorption rate at 273 K and a small amount of H_2 is observed to desorb at 407 K following cyclohexane desorption. The EELS study of Demuth et al. has indicated that cyclohexane dehydrogenates to benzene on Pt(111) above 200 K[1]. We suspect that this H_2 signal at higher temperature is due to decomposition of cyclohexane and that the conversion of cyclohexane to benzene is competitive with cyclohexane desorption. Using EELS, Lehwald and Ibach[15] also found that cyclohexane was partially dehydrogenated on a stepped Ni(111) surface at 150 K, and upon warming from 150 to 260 K the cyclohexane was fully converted to π-bonded benzene. It is noted that these authors found all cyclohexane normal modes active, which is, by the dipole selection rules, consistent with 1-fold, 2-fold, and 3-fold adsorption of the chair form.

The hydrogen atoms' nearness to the surface should facilitate the CH bond cleavage. When the triangular array of lower axial CH bonds is placed in the 2-fold bridge site on Pt(111) as in Figure 3, the molecule allows the CH bonds to point at the surface metal atoms for activation. A lower axial CH bond of the c-C_6H_{12} molecule is stretched 0.6 Å toward the metal atom to reach the transition state that determines the calculated activation barrier of 1.25 eV. In the transition-state structure the stretching CH bond bends up by 15° to aim at the surface metal atom and the equatorial CH bond of the same carbon shrinks 0.02 Å and bends down by 2°. In our model no optimization is done for other variables of the structure. The barrier is low because CH σ donation to the surface through C–H–Pt three-center bonding stabilizes the transition state as shown in Figure 6. The antibonding counterpart to this orbital lies high and empty. This latter feature is important for σ stabilization in the transition state. The 3-centered CH σ donation activation phenomenon has been studied in earlier ASED–MO studies of various transition metals[4-8] and metal oxides.[9] In the case of metals, the antibonding counterpart orbitals donate their electrons into the partially-filled valence d band or conduction band before the transition state is reached, while on oxides photoactivation is possible.

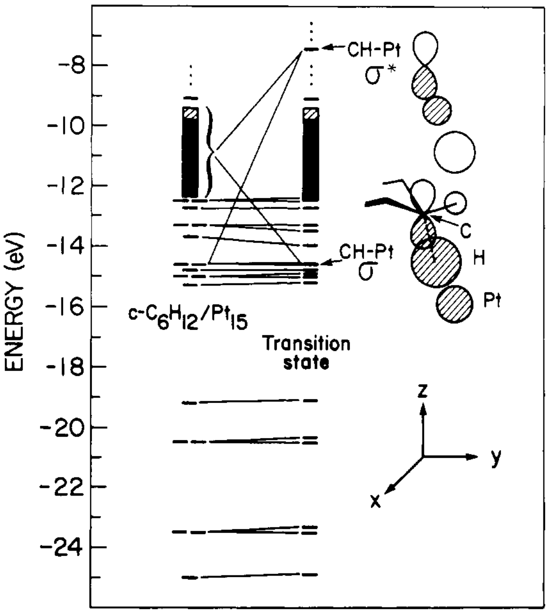

Figure 6. CH σ donation bonds stabilizing the transfer of H from the cyclohexane molecule adsorbed in the 2-fold site.

Table III. Binding Energies (BE) and Heights for Various Adsorbates on 2-fold Site and Activation Barriers (EA) for H Transfer from Them[a]

	adsorbate			
	c-C_6H_{12}	c-C_6H_{11}	c-C_6H_{10}	c-C_6H_9
BE (eV)	0.36			3.80
C–surface distance (Å)	3.23 (3.77)	3.13, 3.09 (3.67)	2.68, 2.64 (3.22)	2.01 (2.59)
ΔCH (Å)	0.6	0.6	0.4	0.4
EA (eV)	1.25	1.16	0.74	0.43

[a] CH are CH bond stretches from the adsorbed structure. Values in parentheses in C–surface distances are defined in Table II, the second entry being for the CH group.

The activation barriers for a second and a third hydrogen transfer from the lower axial CH bonds are calculated to be 1.16 and 0.74 eV, respectively (Table III). These barriers are lower because the ring relaxes closer to the model surface due to the metal–carbon bonding and this forces remaining axial CH bonds into the surface activating them. Once the loss of the first three hydrogen atoms has happened, the c-C_6H_9 molecule approaches very close to the surface to form three M–C bonds and at this time the equatorial CH bonds on alternate carbons become activated and the first one breaks with a low barrier of 0.43 eV. At this point the chair-shaped C_6 ring will begin to flatten in shape and the other two hydrogen atoms will come off with low barriers to form planar benzene; this last step was not calculated. According to an earlier ASED–MO study,[16] the benzene which forms

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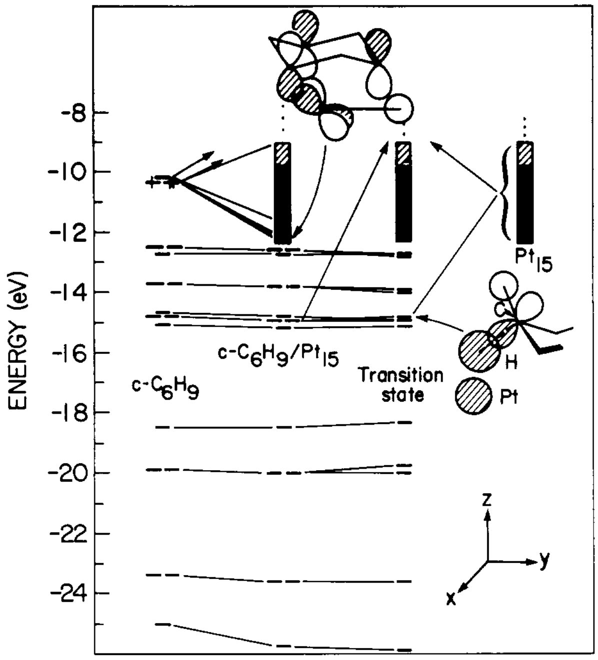

Figure 7. Orbital energy level correlation diagram for the bonding of c-C_6H_9 to the 2-fold site and for CH σ donation stabilizations aiding the H transfer to the surface.

will bond most strongly at a 3-fold site, that is, with the center of the C_6 ring over a 3-fold hole. The initial removal of a hydrogen atom from cyclohexane is the slowest step in the dehydrogenation process followed by the formation of partially dehydrogenated intermediate, c-C_6H_9, which loses three more H atoms even more easily.

In the chemisorbed c-C_6H_9 molecule all CC bonds and the CH bonds of the CH groups shrink 0.04 Å. The chemisorption bonding is due to the mixing of carbon p orbitals of the CH groups with the surface metal s–d band orbitals. One such orbital is sketched in Figure 7. The binding energy is calculated to be 3.8 eV and this value is quite large, compared to that of c-C_6H_{12}. When an equatorial CH bond of the adsorbed c-C_6H_9 molecule is stretched 0.4 Å to the transition state, the emptying of the high-lying CH–M σ^* orbital gives rise to the significant stabilization by means of the CH donation bond to the metal s–d band in the transition state as discussed above. This stabilization is also illustrated in Figure 7.

Conclusions

We have demonstrated that the CH vibrational mode softening is greatest for those CH bonds that point toward surface atoms and the intensity of signal is proportional to the number of these bonds. We also note that these bonds have low dissociation barriers and that CH activation is expected to be strongest for hydrocarbon molecules which adsorb with CH bonds directed toward the surface to make a nearly linear M–H–C transition-state structure. The likelihood for this happening depends on the structure and orientation of the hydrocarbon molecule above the surface. In the case of cyclohexane and cyclopentane 3 CH bonds are weakened on Pt(111) because of the match to the surface atom arrangement. For cyclooctane perhaps one or at most two CH bonds are activated. The dehydrogenation of cyclohexane to benzene is found to proceed in an accelerating way: as dehydrogenation takes place, strong Pt–C bonds draw the hydrocarbon skeleton closer to the surface, further activating the remaining axial and then equatorial CH bonds in proximity to the surface. Our findings for cyclohexane adsorption structure and CH bond weakening on Pt(111) are not qualitatively dependent on the transition-metal d orbital size or ionization potential or d band electron occupation, which explains why our findings are consistent with the limited experimentally available structure data for cyclohexane adsorbed on isostructural surfaces of other metals. As discussed elsewhere,[8] the CH bond activation should be strongest for transition metals with the largest valence d orbitals.

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Registry No. Pt, 7440-06-4; cyclohexane, 110-82-7; benzene, 71-43-2.