J. Am. Chem. Soc. 1984, 106, 6597–6600

Propylene Adsorption and α-Hydrogen Abstraction on Pt(111). Mechanism for 1,3-Sigmatropic Shifts

A. B. Anderson,* D. B. Kang, and Y. Kim

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 23, 1984*

Abstract: We find, in an atom superposition and electron delocalization molecular orbital study, propylene coordinates through the olefinic end preferentially to a di-σ bridging site on a two-layer Pt_{18} cluster model of the Pt(111) surface. Metal donation into the π^* orbital of propylene stretches the double bond, and the olefinic CH and methyl CC bonds bend away from the surface. When the methyl group is properly rotated so that a CH bond points at a surface atom, a net activation energy of 0.7 eV is found for hydrogen abstraction. The products, allyl and hydrogen, are slightly more stable. Activation is a consequence of CH σ bond stabilization in the transition state by overlap with and donation into the higher lying platinum s–d band. CH σ^* participation is relatively minor. Allyl prefers the same di-σ coordination as propylene. A 1,3-sigmatropic hydrogen shift is expected to occur most readily following a shifting motion of allyl so that the surface hydrogen can bond to the other end. The suprafacial intramolecular shift is found to be symmetry forbidden even in chemisorbed propylene, with a barrier of 3.4 eV, though the symmetric $CH_2CH_2CH_2$ trimethylene intermediate shows stability comparable to adsorbed propylene. A barrier of 0.8 eV is determined for hydrogen abstraction from the central methylene group, and a 0.9-eV barrier is found for olefinic hydrogen abstraction. These results are related to the experimental catalysis and surface science literature and to past theoretical studies of AH bond activation.

Suprafacial 1,3-sigmatropic shifts are Woodward–Hoffmann forbidden,[1,2] yet on metal catalysts product distributions imply an intramolecular shift mechanism.[3,4] More recent stereochemical studies have shown the mechanism cannot be intramolecular in certain steroids.[5] An extended Hückel analysis has suggested transition-metal centers might stabilize the suprafacial 1,3-shift mechanism, but the structure model for allyl was a crude planar one.[6] In this paper we examine methyl α-hydrogen bond breaking in propylene adsorbed to the (111) surface of platinum using a two-layer thick Pt_{18} cluster model (Figure 1) and the atom superposition and electron delocalization molecular orbital theory.[7] In this study adsorbate molecular structures are optimized and our results are, as a result, significantly different from those of the earlier study.[6] We find the suprafacial 1,3 shift remains forbidden when propylene is adsorbed on the surface and that the intramolecular shift observed in catalytic studies[3,4] must involve coadsorbed allyl and a hydrogen atom. We also find low activation energies for trimethylene formation and for olefinic hydrogen abstraction. Our calculated energies and structure parameters are semiquantitative, as are those of most other methods, and the proper emphasis is on changes in properties rather than their absolute magnitudes.

Propylene Adsorption and α-Hydrogen Abstraction on Pt(111)

Propylene favors di-σ coördination with the CC double bond parallel to the surface model and stretched 0.27 Å (Figure 2). Full structure optimizations at μ-coordination sites indicate no adsorption, and at π sites adsorption is about a third as strong as in the di-σ site. It may be noted that with the present parameters our calculations systematically overestimate CH bonds by 0.1 Å and CC single and double bonds by 0.2 and 0.15 Å, respectively, though they are quite close for diatomic C_2.[8] Consequently, the figure shows changes in CH and CC bond lengths due to adsorption. The methyl carbon is tilted up away from the surface as are the olefinic CH bonds. Bonding to the surface is a result of propylene π-orbital stabilization due to mixing with Pt s–d band orgitals and Pt band stabilization due to mixing with the higher lying empty π^* orbital. These are, respectively, the expected donation and back-bonding interactions. Figure 3 shows the associated energy levels and π, π^*, and σ_p hybridization and mixing with metal orbitals on adsorption. Though the 0.27-Å CC stretch causes the σ_p level to shift up several tenths of an electron volt, its bond to the surface pushes it down to nearly its original position. The π–π^* spitting is reduced due to its stretch, but bonding to the surface stabilizes the orbital to a position below its original position. The π^* orbial mixes strongly at the bottom of the s–d band. Orbital energy levels with 0.2 electron or greater population on propylene are shown in the figure; weaker mixings are found throughout the metal band. The π + metal antibonding orbital lies high and is empty, so as not to cancel the π-donation bond. The calculated binding energy of 2.1 eV is higher than estimated experimentally,[9] but it will reduce when adsorbate repulsions are taken into account, as we have done previously for acetylene.[7b] Our following discussions will center on changes in adsorbate energies just as we discuss changes in adsorbate bond lengths, as these quantities are subject to small systematic errors, but their changes are significant and subject to interpretation.

On rotating the methyl group so that a CH bond points at a surface metal atom, it may be stretched 0.5 Å to a transition state for α-hydrogen abstraction shown in Figure 4. This transition state is a multidimensional saddle point, and the overall geometry is given in the figure, where it may be noted the methyl carbon tilts 6° toward the surface. The α-hydrogen abstraction barrier is calculated to be 0.7 eV, much less than 4.5 eV calculated for the gas-phase propylene → allyl + hydrogen reaction. The barrier is low because of σ donation to the surface in 3-centered C–H–Pt bonding orbitals shown in Figure 5. For comparison, propylene levels in the transition-state structure without the surface cluster are given in the third energy level column in the figure, showing clearly the importance of the σ stabilization in the transition state. The π-chemisorption stabilization is also evident. CH σ^* mixing is minor and only one half-filled orbital at the top of the half-filled Pt band has σ^* character; the criterion for showing CH levels is 0.1 electron or more in the CH orbital. Main CH σ^* orbitals lie high and empty. Adsorbed allyl and hydrogen are comparable in stability to adsorbed propylene in our calculations, about 0.1 eV more stable. Various possible hydrogen-binding sites are close

---

[1] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[2] For additional discussion, see Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142.

[3] Smith, G. V; Swoap, J. R. *J. Org. Chem.* **1966**, *31*, 3904.

[4] Touroude, R.; Hilaire, L.; Gault, F. G. *J. Catal.* **1974**, *32*, 279 and references therein.

[5] Ku, V.; Palmer, J.; Siegel, S.; Clough, R. *J. Catal.* **1976**, *44*, 449.

[6] Anderson, A. B. *Chem. Phys. Lett.* **1975**, *35*, 498.

[7] For parameters and examples of the application of this technique to acetylene adsorption on platinum surfaces, see: (a) Anderson, A. B.; Hubbard, A. T. *Surf. Sci.* **1980**, *99*, 384. (b) Mehandru, S. P.; Anderson, A. B. *Appl. Surf. Sci.*, in press.

[8] Anderson, A. B. *J. Chem. Phys.* **1975**, *63*, 4430.

[9] Salmerón, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.

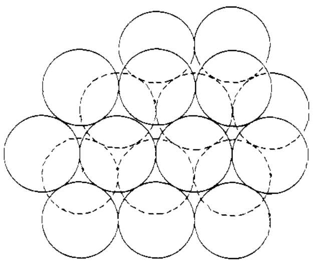
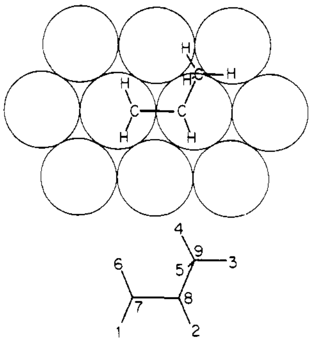


Figure 1. Pt_{18} cluster used in this study.



ANGLE (DEG)		ΔR (Å)	
176	113	78	0 27
178	110	89	0.01
678	110	71	-0.01
17S	25	76	-0 01
67S	25	82	-0 01
782	111	93	0 00
28S	27	94	0.00
789	111	95	0 00
98S	30		
893	107		
894	107		
895	107		
59S	74		
49S	-23		
39S	- 8		

Figure 2. Structure of chemisorbed propylene. ΔR are bond length changes with respect to the gas phase. The height of the double bond, h, is 2.02 Å. Angles are optimized in 2–3-deg increments. Bond lengths are optimized in 0.01-Å increments.

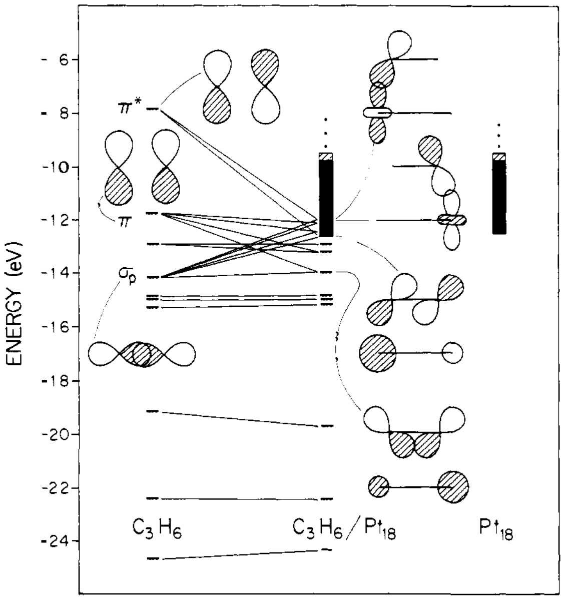
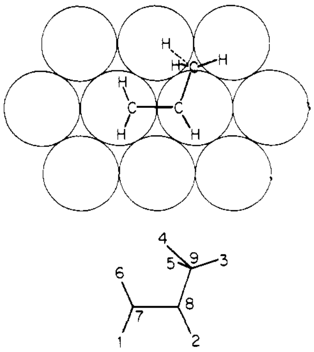


Figure 3. Bonding between propylene and Pt_{18}; the structure is in Figure 2. The cross-hatched band stands for 10 unpaired electrons at the top of the d band, see ref 7.



ANGLE (DEG)		ΔR (Å)	
176	114	78	0.00
178	108	89	-0 04
678	110	71	0 00
17S	26	76	-0 01
67S	26	82	0 00
782	111	93	-0 03
28S	29	94	0 50
789	105	95	-0 03
98S	24		
893	115		
894	93		
895	115		
59S	61		
49S	-41		
39S	-14		

Figure 4. As in Figure 2 for the α-hydrogen-abstraction transition state. ΔR with respect to adsorbed propylene.

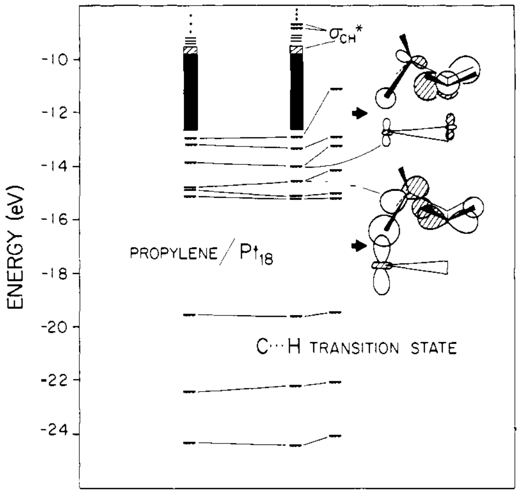


Figure 5. CH σ-donation stabilizations responsible for α-hydrogen activation. Levels at the far right are for the transition-state structure but with the surface omitted.

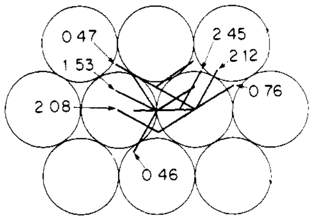
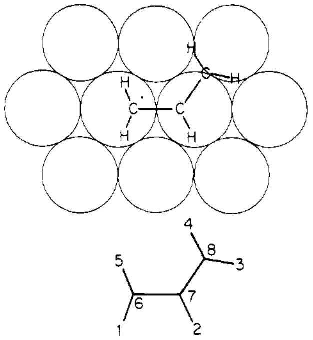


Figure 6. Various sites for allyl and respective adsorption energies.



ANGLE (DEG)		ΔR (Å)	
165	114	67	-0 02
167	108	78	-0 08
567	110	61	0.00
16S	25	65	0.00
56S	25	72	0 00
672	112	83	-0 03
27S	30	84	-0 04
678	125		
384	119		
783	112		
784	117		
38S	21		
48S	13		

Figure 7. As in Figure 2 for the di-σ-coordinated allyl. ΔR with respect to adsorbed propylene. The height is 2.00 Å.

in energy, indicating adsorbed hydrogen atoms are thermally very mobile.

Allyl Binding and Mechanism for the 1,3-Sigmatropic Shift

We find allyl prefers the same di-σ binding site as propylene. Figure 6 shows various structures, all of which have allyl fully otpimized, and their binding energies. The structure of di-σ allyl is in Figure 7. The di-σ CC bond is 0.16 Å longer than in the gas-phase allyl, and the other CC bond is 0.10 Å longer. The allyl–surface bond includes π_1 donation and back-bonding into the π_2 and π_3 orbitals as shown in Figure 8. The π_2 and π_3 orbitals hybridize in such a way as to give the second CC bond additional π character.

A 1,3-hydrogen shift will be the outcome of the abstracted hydrogen bonding to the other end carbon atom. This can occur if allyl shifts so that the center and right-hand carbon atoms are di-σ coordinated to the surface, allowing the formation of a new π–d surface bond. The transition state for this shift is symmetric and is shown in Figure 9. There is a small 0.3-eV barrier for the shift. Once allyl has shifted, the hydrogen atom on the surface can bond to the carbon atom at the other end which is now not part of the CC di-σ bond to the surface. The pathway and energetics for this are the inverse of the original α-hydrogen-abstraction step.

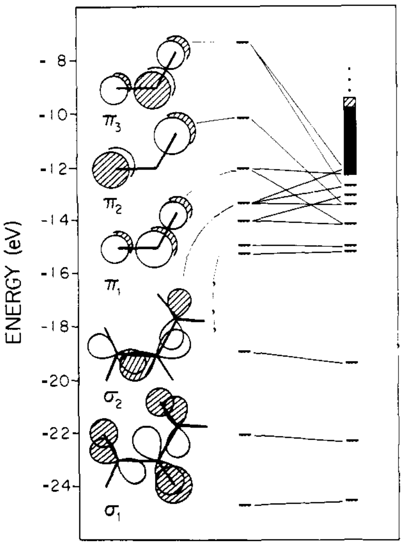
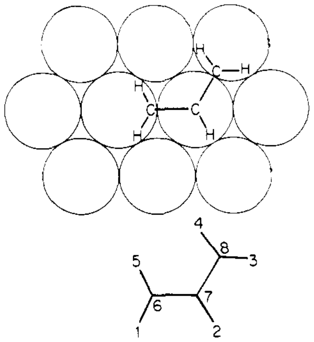
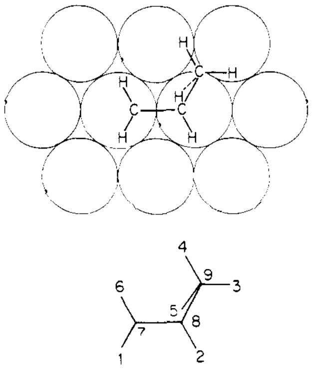


Figure 8. Bonding between allyl and Pt_{18}; the structure is in Figure 7.



ANGLE	(DEG)	ΔR	(Å)
165	116	67	-005
167	116	78	0.01
567	116	61	-001
16S	25	65	-001
56S	25	72	0.00
672	116	83	000
27S	25	84	001
67S	5		
87S	5		
678	117		
384	116		
783	116		
784	116		
38S	25		
48S	25		

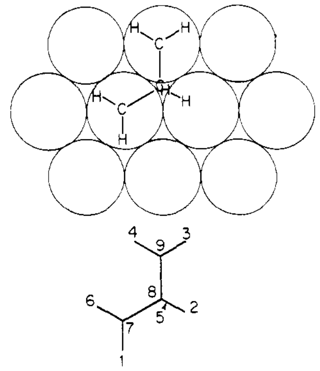
Figure 9. As in Figure 2 for allyl shifting through the transition state. ΔR with respect to adsorbed allyl in the di-σ site. The height of the end C is 2.10 Å and that of the central C is 1.97 Å.



ANGLE	(DEG)	ΔR	(Å)
176	113	78	000
178	110	89	000
678	110	71	000
17S	25	76	000
67S	25	82	000
782	111	93	-003
28S	25	94	-003
789	114	95	025
98S	22		
893	112		
894	112		
895	53		
59S	30		
49S	-16		
39S	6		

Figure 10. As in Figure 2 for the suprafacial 1,3-shift transition state. ΔR with respect to adsorbed propylene.

A suprafacial mechanism has been tried. A methyl CH bond pointing away from the surface was bent back toward the central carbon atom, but the lowest energy barrier that could be found was 3.4 eV for the transition state shown in Figure 10. The transferring hydrogen atom is 1.45 Å from the carbon atoms it bridges. The lower value of the earlier model study[6] was caused by forcing the allylic part of the system to be planar on the metal surface, which induced stabilization in it in the transition state. The stabilization resulted from metal donation to and stabilization of the π_2 orbital. This occurred despite the lack of overlap of the shifting hydrogen with the central carbon atom. In the present work the 1s orbital of this hydrogen atom is predominately involved in mixing with the π_1 orbital. In agreement with the Woodward–Hoffmann theory, this stabilization is insufficient to make the suprafacial pathway kinetically allowed, even on the Pt(111) surface. However, it is worth exploring the possibility of a suprafacial 1,3-hydrogen shift in systems such as pinenes where the olefinic and allylic structures are necessarily relatively planar, thereby approximating the prior model study.[6] (We thank a reviewer for suggesting this experiment.)



ANGLE	(DEG)	ΔR	(Å)
176	114	78	-003
178	110	89	003
678	110	71	-001
17S	21	72	-001
67S	15	82	001
782	108	85	0.04
87S	16	93	000
789	115	94	001
589	109		
582	112		

Figure 11. As in Figure 2 for trimethylene. ΔR with respect to di-σ allyl. The height of the end C is 2.07 Å and that of the central C is 2.53 Å.

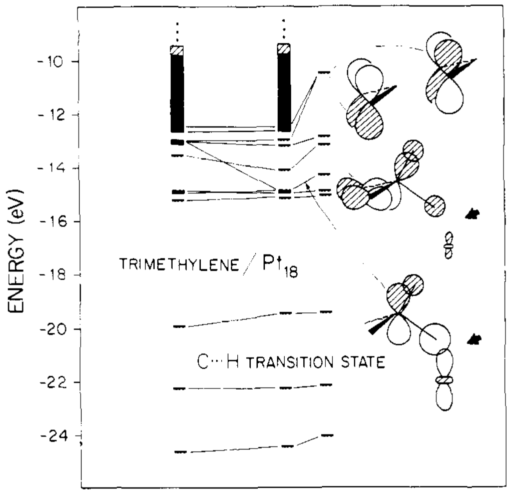


Figure 12. CHσ-donation stabilizations responsible for central trimethylene CH activation. Levels to the right are for the transition-state structure but with the surface omitted.

Trimethylene has been studied theoretically in the past as an intermediate in cyclopropane isomerization.[10-12] It is of interest to examine its stability on the platinum surface. We find trimethylene is a stable molecule with the two end carbon atoms σ bonded to two surface-metal atoms. The trimethylene structure (Figure 11) is similar to that of propane, and adsorbed trimethylene is calculated to be 0.1 eV more stable than adsorbed propylene. The CC bonds are nearly equal to the single bond length and the Pt–C bonds at 2.07 Å are equal to the sum of the covalent radii of platinum and carbon atoms. The energy barrier for removing a hydrogen atom in the central methylene group so that a 3-centered transition state is formed between C, H, and the nearest surface Pt atom is calculated to be 0.8 eV with a 0.6-Å CH stretch. As for α-hydrogen abstraction, CH σ donation to the surface activates this process as shown in Figure 12, where the nature of the carbon σ bonding to the surface is also evident.

From the above it may be concluded that propylene, allyl + hydrogen, and trimethylene are all nearly equally stable on the Pt(111) surface. The reversible α-hydrogen-abstraction barrier is low at 0.7 eV, and the barrier to the reaction allyl + H → trimethylene on Pt(111) is somewhat greater, but still low. The energy required to shift allyl to a neighboring di-σ position so that

---

(10) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(11) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.

(12) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 638.

hydrogen can bind at the other end is very small at 0.3 eV. It is possible that trimethylene would form occassionally following α-hydrogen abstraction, but it is much more likely that the hydrogen atom would, if it is constrained to remain in the catalytically active surface region, as seems to be the case on platinum,[1] reduced platinum oxide,[1] and palladium surfaces,[1,2,5] rejoin allyl at one end or the other, leading to a mixture of the original propylene and its 1,3-shifted isomer on desorption. And, finally, the suprafacial gas-phase 1,3-hydrogen shift, which is Woodward–Hoffmann forbidden, is also forbidden on platinum and probably other transition-metal surfaces as well.

Olefinic CH Activation

Overtone vibrational excitations of CH bonds in propylene, when interpreted in the local mode vibrational framework, indicate methyl CH bonds are 0.4 eV or more weaker than the olefinic CH bonds and the out-of-plane methyl CH bonds are ~0.4 eV weaker than the in-plane methyl CH bond.[13] Such differences translate into relative bond strength differences ocurring at CH bond scission transition states where CH bonds are stretched about 0.5 Å and relaxations in the molecule are not yet large. The out-of-plane methyl CH bonds are weaker than the in-plane one because the π orbital becomes stabilized by a hybridized p orbital on the methyl carbon as the CH bond is stretched.[14] It may be noted that bond strengths determined by kinetic methods, and hence including full relaxation, show similar behavior. The CH bond in methane is 0.2-eV weaker than an olefinic CH bond, and the H-allyl bond is 0.65-eV weaker than the CH bond in methane.[15] The weakness of the H-allyl bond is due to the stabilization caused by π delocalization in allyl. In our calculations the π-orbital stabilization is 0.4 eV, and since the orbital is doubly filled, 0.8 eV is the stability gain due to π delocalization when an α-hydrogen is abstracted from propylene. This compares well with 0.65 eV from experiment.

Having established that methyl CH bonds in propylene, particularly out-of-plane ones, are 0.85-eV weaker than olefinic CH bonds, it is no surprise that when toluene is adsorbed on Ni(111) the methyl CH bonds break first according to a thermal desorption mass spectroscopic study.[16] On Pt(111) the aliphatic CH bonds appear to break first, at a temperature around 343 K.[17] Propylene has been examined on Pt(111), and from a thermal desorption study a barrier of 0.7–1.0 eV has been estimated for the first hydrogen elimination, which occurrs at 296 K.[8] There is a shoulder at 328 K and then a peak at 436 K when 4 hydrogen atoms are eliminated with a barrier of 1.0–1.2 eV.[8] The remaining CH species dehydrogenate at higher temperatures.

HD exchange in propylene is much greater than for adsorbed molecular acetylene and ethylene and as many as three deuterium atoms can be added.[8] This is consistent with the readily reversible α-hydrogen abstraction we predict for propylene, provided the allylic intermediate does not shift on the surface. On the basis of these results one suspects the 296 K hydrogen desorption peak is due to α-hydrogen abstraction, not olefinic hydrogen abstraction as implied by comparison with ethylene in ref 14. The shoulder at 328 K may represent the loss of hydrogen from a small fraction of adsorbed allyl molecules accompanying rearrangements which yield adsorbed propylidyne, CCH_2CH_3. We have examined hydrogen abstraction from ethylene on this surface and find, with the methylene groups twisted about 30° and CC axis rotated atoub 20°, a barrier 0.2 eV higher than that for α-hydrogen abstraction, about 0.9 eV in our approximate calculations with a CH stretch of 0.4 Å. Thus propylidyne is likely to form from allyl by means of 1,2-hydrogen shifts: $CH_2CHCH_2 \rightarrow CHCH_2CH_2 \rightarrow CHCHCH_3 \rightarrow CCH_2CH_3$. A single such shift can also account for ethylidyne[8] formation from adsorbed ethylene following the first hydrogen abstraction and vinylidene[14] formation from acetylene. Work on 1,2-hydrogen shifts is underway in our laboratory.

Concluding Comments

This study and other recent studies[16,18,19] show that aliphatic, olefinic, and acetylenic CH bonds are readily activated by platinum (and iron) surfaces. The prerequisite requirement for activation is placing the CH bond in close proximity to the metal surface so that at the transition state the CH σ-bonding orbital can σ donate to a metal atom or atoms, resulting in a stabilized tansition state. This condition has also been found important for OH bond scission in chemisorbed water and hydroxyl[20] and HCl bond scission in chemisorbed HCl.[21] Mixing of the CH σ^* orbital is relatively weak at the transition state except on electropositive metals.[22] While the examples studied so far have the hydrogen-containing species strongly chemisorbed to the metal surfaces via donation and back-bonding interactions involving C, O, and Cl, it is expected that alkanes will experience similar CH activation. Since light alkanes only weakly chemisorb,[19b] sufficient temperature and pressure will be required to ensure collisions with the proper CH bond orientation to have activation a frequent event. Finally, our study shows the suprafacial 1,3-hydrogen shift remains symmetry forbidden in propylene chemisorbed to Pt(111), as it is for gas-phase propylene. This result concurs with the most recent stereochemical studies of catalyzed 1,3 shifts of ref 5.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Standard Oil Company of Ohio for their support.

Registry No. Propylene, 115-07-1.

---

(13) Fang, H. L.; Swofford, R. L. *Appl. Opt.* **1982**, *21*, 55.

(14) Anderson, A. B.; Gervasio, D.; Fang, H. L.; Swofford, R. L., unpublished.

(15) "CRC Handbook of Chemistry and Physics", 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1980; p F-231.

(16) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773.

(17) Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534.

(18) Anderson, A. B.; Mehandru, S. P. *Surf. Sci.* **1984**, *136*, 398.

(19) (a) Anderson, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 696. (b) Rhodin, T. N.; Brucker, C. F.; Anderson, A. B. *J. Phys. Chem.* **1978**, *82*, 894.

(20) Anderson, A. B. *Surf. Sci.* **1981**, *105*, 159.

(21) Debnath, N. C. Anderson, A. B. *J. Vac. Sci. Technol.* **1982**, *21*, 945.

(22) Anderson, A. B.; Ray, N. K. *J. Phys. Chem.* **1982**, *86*, 488.