of the S_3 state is greatly displaced from that of the ground state. The $S_3 \leftarrow S_0$ transition is calculated to be relatively intense and to be within 0.2 eV of $S_2 \leftarrow S_0$. The height of the calculated ethylenic torsional barrier for S_1 suggests that photoisomerization will not occur in the S_1 state without a large degree of excess vibrational energy. At such energies direct excitation of the higher states (S_2 and S_3), which have larger absorption cross-sections,

may in fact be responsible for excited-state cis–trans isomerization.

Registry No. Styrene, 100-42-5.

Dependence of CC and CH Bond Activation on d Band Position: Acetylene on Pt(111) and Fe(100). An Electrochemical Model

S. P. Mehandru and Alfred B. Anderson*

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. Received January 20, 1984

Abstract: A study is made of the dependence of CC and CH bond activation energies in acetylene on d band positions when bonded to cluster models of Pt(111) and Fe(100) surfaces. In their normal positions, these bands lie in energy between the acetylene-filled π and empty π^* orbitals. On shifting down (anodic), acetylene π donation to the metals increases and acetylene adsorption energies increase while CC and CH bond scission barriers decrease. On shifting up (cathodic), metal donation to acetylene orbitals increases, also leading to increased acetylene adsorption energies and increased CC and CH activation toward scission. The CC and CH σ and σ^* orbitals also play a role in stabilizing the bond scission transition states. These results, based on atom superposition and electron delocalization molecular orbital theory, are used as a basis for discussing experimental electrochemical work from the literature.

Introduction

In recent studies we have identified a structure effect which determines favored binding sites and influences the distortions of acetylene chemisorbed on (111), (110), and (100) surfaces of iron[1] and platinum.[2] In essence, the carbon atoms in acetylene form as many strong bonds to as many surface metal atoms as possible. When the metal atoms are relatively far apart, as at the 4-fold site of Fe(100) (Figure 1), the adsorbed acetylene molecule is strongly distorted, with a large CC stretch and a large bending of the CH bonds away from the surface. Furthermore, the CC bond is highly activated toward dissociation, which is confirmed by the observed dissociation of acetylene on Fe(100) at 98 K.[3] By contrast, on Pt(111) the metal atoms in the favored triangular site (Figure 1) are relatively close together and the distortions and activation of an adsorbed acetylene molecule are predicted to be less, which is in agreement with experiment.[4] It is of interest to explore the effects of other physical variables in metal surfaces on acetylene adsorption. One such variable is d orbital size. The spacial extents of Fe 3d and Pt 5d orbitals are similar, so an examination of acetylene adsorption on metals with large d orbitals, such as titanium, and small d orbitals, such as copper, would elucidate the importance of carbon p–metal d overlaps. This will not be treated in the present work but is reserved for future studies.[5] Another variable is the metal d band occupation. Again, an explicit study will be reserved for the future,

though it may be noted that the orbitals involved in the metal-acetylene bond lie beneath the d band in the iron and platinum examples we have already treated. That is, major acetylene-to-metal π donation and metal-to-π^* back-donation orbitals that are occupied have energies near the bottom or beneath the d band. The major acetylene π plus metal antibonding counterparts lie above the d band and are empty. Thus, d electron count may be a relatively unimportant variable for acetylene adsorption. The final variable to consider is the metal atom d electron ionization potential, that is, the d band position. This is the variable treated in the present study. It is expected that as the d band moves down in energy, acetylene π donation to the metal will increase and metal back-donation to the acetylene π^* orbitals will decrease. What will be the effects of d band position on acetylene geometry and CC bond activation? This study attempts to answer this question in the case of acetylene on Fe(100) and Pt(111) surfaces. In addition, we examine the influence of d band position on CH bond activation. These two surfaces are chosen because acetylene is known to dissociate on clean Fe(100) at monolayer coverage in high vacuum at only 98 K, covering the surface with CH fragments.[3] On Pt(111), the acetylene molecule is stable up to <350 K, and at higher temperature it rearranges and may become hydrogenated.[4]

Our recent studies[1,2a] of acetylene adsorption on the Fe and Pt(111), -(110), and -(100) surfaces show that in each case acetylene π orbitals give rise to bands on adsorption. In the case of the iron surfaces, the π orbital energy levels are stabilized by π donation to the metal d orbitals and are shifted to a position ~ 1 eV beneath the bottom of the Fe s–d band for Fe_5 and Fe_{21} clusters modeling the (100) surface.[1] This position of the π band relative to the Fe band is in close agreement with photoemission studies.[3] For Pt(111), we have found[2a] a similar π stabilization on adsorption, but in this case the π band is merged into the bottom of the Pt s–d band. This also is in agreement with the results of photoemission studies.[6] On this basis it is reasonable to assume

(1) Anderson, A. B.; Mehandru, S. P. *Surf. Sci.* **1984**, *136*, 398.
(2) (a) Mehandru, S. P.; Anderson, A. B. *Appl. Surf. Sci.* in press. (b) Anderson, A. B.; Hubbard, A. T. *Surf. Sci.* **1980**, *99*, 384.
(3) Rhodin, T. N.; Brucker, C. F.; Anderson, A. B. *J. Phys. Chem.* **1978**, *82*, 894.
(4) (a) Demuth, J. E. *Surf. Sci.* **1979**, *80*, 367. (b) Ibach, H.; Lehwald, S. *J. Vacuum Sci. Technol.* **1978**, *15*, 407. (c) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180.
(5) Work in progress shows acetylene dissociated with no activation energy on all sites of V(100).

Table I. Parameters Used in the Calculations for Acetylene Adsorption on Uncharged Pt and Fe Surfaces: Principal Quantum Number (n), Ionization Potential (IP) (in eV), Orbital Exponents (ζ), and Respective Coefficients (c) for Double-ζ, d Functions

atom	s			p			d			
	n	IP	ζ	n	IP	ζ	n	IP	ζ	c
Pt	6	10.00	2.550	6	5.96	2.250	5	10.60	6.013	0.6562
									2.396	0.5711
Fe	4	8.87	1.700	4	4.87	1.400	3	10.00	5.350	0.5366
									1.800	0.6678
C	2	19.00	1.658	2	10.26	1.618				
H	1	12.60	1.200							
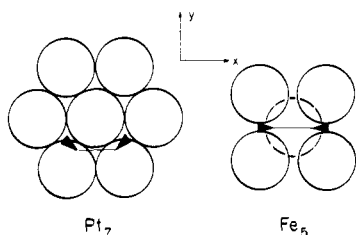
Figure 1. Fe$_5$ model of Fe(100) and Pt$_7$ model of Pt(111) showing respective 4-fold and triangular sites favored for acetylene adsorption.

that the acetylene π and π^* and metal band positions are in their correct relative positions for describing adsorption in a vacuum. Our calculated highest occupied orbitals correspond to ionization potentials 4–5 eV greater than the workfunctions of these metal surfaces. This is because our initial-state calculations omit final-state relaxations which accompany the ionization process from a metal surface.

Shifting the d band is more than a test of the sensitivity of calculated results to atomic parameters. The d ionization potential increases across the first transition series, covering a 4-eV range. Such shifts also occur when a potential is applied to a metal electrode or when electropositive or electronegative atoms are adsorbed on metal surfaces. We have used this technique to explain the potential dependence of AgC and CN vibrational frequencies for cyanide on a silver electrode,[7a] for CO frequencies for carbon monoxide on a platinum electrode,[7b] for the oxidation and reduction of water on an iron electrode,[7c] for the anodic dissolution of an iron electrode,[7d] for the variation in carbon monoxide binding site and vibrational frequency on a Pt(111) surface with coadsorbed potassium,[7e] for the decrease of the adsorption energy of benzene on Pt(111) with coadsorbed potassium,[7f] and for acetylene adsorption and CC bond scission on a Ni(100) electrode.[7g] Thus, the results of the present work may be interpreted to show what will happen to acetylene CC and CH bond activations on Fe(100) and Pt(111) surfaces when charged cathodically and anodically in an electrolyte.

We employ the atom superposition and electron delocalization molecular orbital theory used in past studies. Atomic orbital parameters and ionization potentials are those used previously for acetylene on iron and platinum[1,2] and are given in Table I. We shift metal atom s, p, and d ionization potentials 1 and 2 eV in the anodic and cathodic directions with respect to values used previously. This serves to establish trends. In aqueous electrolytes, H_2 reduction and O_2 oxidation reactions decrease the available potential range to less than 2 V. Furthermore, even though the first transition series shows a 4-eV range in ionization potentials, in practice the effective range will be less because of the effect of charge self-consistency. In the ASED-MO theory, the ionization potentials are determined by performing calculations of

Table II. Calculated Binding Energy of Acetylene (BE$_{C_2H_2}$), Height Above the Surface (h), CH Bending Angle Away from the Surface (θ), CC Bond Stretch (ΔCC), Tilt of CCH Plane Relative to Surface Normal, Displacement Away from the 1-Fold Site of the Central Platinum Atom (D), and Charges on the Adsorbed Acetylene at the Δ Site of the Pt$_7$ Model of the Pt(111) Surface at Several Values for d Band Shifts (Electrode Potentials)

	potential, V				
	−2	−1	0	+1	+2
BE$_{C_2H_2}$, eV	3.90	2.35	1.65	1.78	2.75
h, Å	1.55	1.55	1.55	1.60	1.60
θ, deg	55	55	55	55	50
ΔCC, Å	0.26	0.24	0.24	0.24	0.24
tilt, deg	20	20	20	20	20
D, Å	1.30	1.34	1.38	1.40	1.44
C_2H_2 charge	−1.85	−1.09	−0.37	0.41	1.19
H charge	−0.01	−0.01	−0.00	0.01	0.02

bond lengths, force constants, and charge separations in MC diatomic species. The valence ionization potentials of M are increased in 0.5-eV increments, and the valence ionization potentials of C are simultaneously decreased in 0.5-eV increments until the charge separation is close to that predicted by Pauling's ionicity relationship. In the case of platinum and iron, the increase is 1 eV. For metals at the left-hand side of the transition series, the increase will be up to 2 or 3 eV.[5] Thus, shifts in metal valence ionization potentials over roughly a 2-eV range will apply to the establishment of trends across the transition series. As will be seen below, larger shifts produce excessively large and unrealistic transfers of charge between acetylene and the metal surfaces; however, the results of such large shifts are included to provide verification for the trends observed over the narrower physically significant range. The previous work gives a detailed discussion of the bonding of acetylene to Fe(100) and Pt(111) within the framework of the ASED-MO theory.[1,2] In this theory the molecular binding energy is a sum of a pairwise atom superposition repulsive energy and an electron delocalization energy which is approximated by a one-electron molecular orbital energy. As was shown, changes in the atom superposition energy play a critical role in determining the structure, stability, and activation of adsorbed acetylene.[1,2] However, molecular orbital bonding theory is sufficient for understanding the acetylene–surface interactions. Consequently we explain the present results in terms of changes in acetylene–metal orbital overlaps and stabilizations as functions of d band positions. The Fe$_5$ and Pt$_7$ cluster models of Fe(100) and Pt(111) (Figure 1) are sufficient for establishing resulting changes in acetylene–surface interactions. As shown in our previous work, the use of a larger cluster did not produce notable changes in structures or relative binding or activation energies for acetylene adsorption on the clean metal surfaces. The small clusters have the advantage of economy when a large number of calculations are required, such as in this study. Our cluster models are high-spin so that each d band orbital is occupied by at least one electron. Thus, 12 orbitals at the top of the d band for Fe$_5$ are half-filled, and for Pt$_7$ two are half-filled. This occupation is consistent with the low-field behavior of metal atoms as ligands and with the bulk paramagnetic moments of these metals. Angles are optimized in 5° increments, acetylene height from the surface plane by 0.05-Å increments, acetylene CC bond stretch and lateral position by 0.02 Å. For simplicity, the lengths of the CH bonds are not optimized.

(6) (a) Albert, M. R.; Sneddon, L. G.; Eberhardt, W.; Greuter, F.; Gustafsson, T.; Plummer, E. W. *Surf. Sci.* **1982**, *120*, 19. (b) Fischer, T. E.; Kelemen, S. R.; Bonzel, H. P. *Surf. Sci.* **1977**, *64*, 157.

(7) (a) Anderson, A. B.; Kötz, R.; Yeager, E. *Chem. Phys. Lett.* **1981**, *82*, 130. (b) Ray, N. K.; Anderson, A. B. *J. Phys. Chem.* **1982**, *86*, 4851. (c) Anderson, A. B.; Ray, N. K. *J. Phys. Chem.* **1982**, *86*, 488. (d) Anderson, A. B.; Debnath, N. C. *J. Am. Chem. Soc.* **1983**, *105*, 18. (e) Ray, N. K.; Anderson, A. B. *Surf. Sci.* **1983**, *125*, 803. (f) Anderson, A. B.; McDevitt, M. R.; Urbach, F. L. *Surf. Sci.*, in press. (g) Anderson, A. B. *J. Catal.* **1981**, *67*, 129.
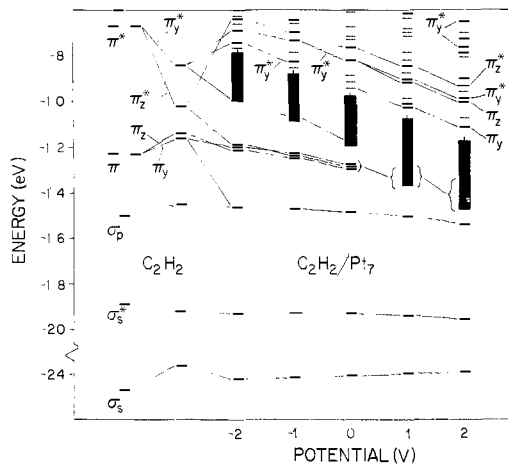
Figure 2. Acetylene plus Pt_7 energy level correlations for various d band positions (electrode potentials). There are two unpaired electrons at the top of the d band. Energy levels for acetylene orbitals with an occupation of 0.2 electron or more are drawn heavy. The first column of C_2H_2 levels is for gas-phase acetylene and the second for distorted acetylene at a −2-V potential but with Pt_7 omitted.

Adsorption and Dissociation of Acetylene on Pt(111) as a Function of d Band Position

The most favored binding site for acetylene chemisorbed on the platinum(111) surface at the five different d band positions considered is the high coordination triangular site with the CC axis parallel to the surface and the CCH plane tilted relative to the surface normal. The calculated results for the binding energy of molecular acetylene, its geometry on adsorption, and the charges on C_2H_2 and H species are given in Table II. Over the range studied, the CC bond stretches by about 0.25 Å and there is a slight increase in the stretch on going in the cathodic direction. This 0.25-Å stretch has also been determined experimentally from a high-resolution electron energy loss vibrational analysis.[4b] The CH bending angle away from the surface decreases and the height of acetylene above the surface increases slightly on going in the anodic direction. This bonding accompanies π donation to the surface and surface back-donation to acetylene π^*, giving rise to ethylenic-like σ bonding orbitals between acetylene and the surface as discussed in our earlier work.[1]

The CCH plane remains tilted by 20° relative to the surface normal. The shift of the CC axis from the 1-fold site of the central platinum atom toward the di-σ bridging site increases in the anodic and decreases in the cathodic direction. The binding energy of acetylene is minimum on the uncharged surface and increases on going anodic or cathodic. At +2-V potential, which, as discussed above, may lie outside the experimentally achievable range, the di-σ bridging site and the triangular site are calculated to be almost equally favored. The orbital correlation diagram for the adsorbed acetylene on the Pt_7 model is given in Figure 2. On going cathodic, as the Pt 5d band moves up, there is progressively more and more interaction with the π^* orbitals of acetylene, giving rise to stronger back-donation from the metal to the π^* orbitals. At the same time, there is decreasing interaction between the d band and the π orbitals. This decreases the π donation to the metal. The sum of these two effects is reflected in the increased charge transfer from the metal to the adsorbate. In the anodic direction, however, the effect is opposite, giving rise to resultant charge depletion from the acetylene molecule. The increase or decrease of charge on acetylene shows a linear relationship with the surface potential as seen in Figure 3. In summary, the strong adsorption in the cathodic direction is caused by increased metal back-bonding into π^* orbitals in acetylene, and the strong adsorption in the anodic direction is caused by increased acetylene π donation to the metal.

As the CC bond of the adsorbed acetylene is stretched on the triangular site of the uncharged Pt model, it dissociates with a calculated activation barrier of 1.2 eV. This represents a strong activation of the carbon–carbon triple bond which has a calculated
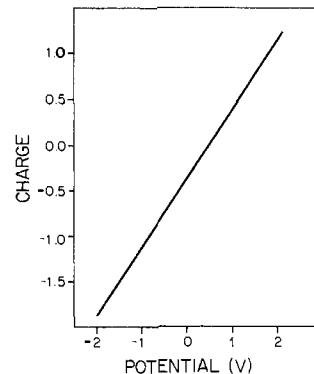

Figure 3. Total charge on acetylene on Pt_7 for various d band positions (electrode potentials).
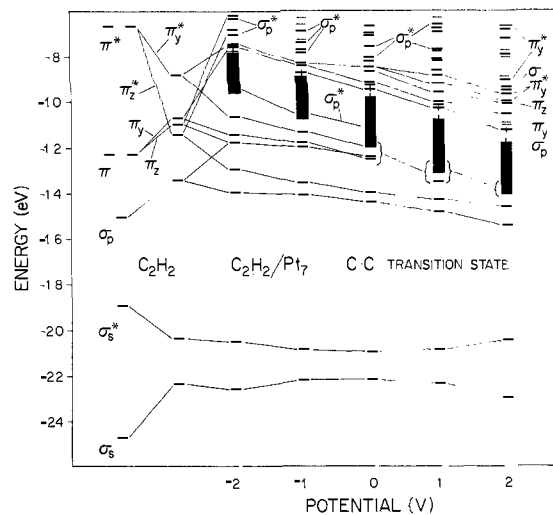

Figure 4. As in Figure 2 for CC bond scission transition state.

Table III. Calculated CC Bond Activation Barrier (EA_{CC}), Binding Energy of CH Fragments[a] (BE_{CH}), ΔCC, θ, h, tilt, and D for Acetylene in the Transition State for CC Bond Activation at the Δ Site of the Pt_7 Model of the Pt(111) Surface at Several Potentials[b]
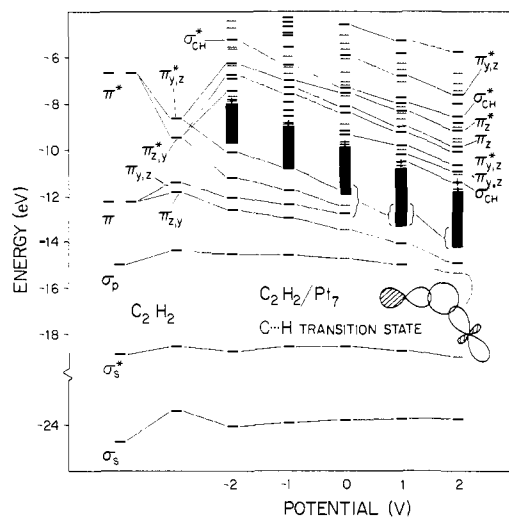
	potential, V				
	−2	−1	0	+1	+2
EA_{CC}, eV	0.44	1.05	1.19	0.87	0.19
BE_{CH}, eV	6.15	4.03	3.10	3.45	4.82
ΔCC, Å	0.52	0.74	0.74	0.64	0.34
θ, deg	70	75	75	75	70
h, Å	1.50	1.50	1.50	1.50	1.55
tilt, deg	20	20	20	20	20
D, Å	1.30	1.34	1.38	1.40	1.44
C_2H_2 charge	−2.59	−1.74	−0.45	0.74	1.58
H charge	0.02	0.03	0.07	0.05	0.05

[a] Relative to the energy of separated Pt_7 model and gas-phase acetylene. [b] See caption to Table II for the definition of these symbols.

strength of 8.3 eV in the gas phase, close to the standard acetylenic triple bond strength of 8.5 eV. It may be noted that on the large 21 atom cluster, the activation barrier increases slightly to 1.3 eV.[2a] On the charged surface, however, whether positive or negative, the activation barrier for CC bond scission decreases (see Table III). In Table III are also given the binding energies of the CH fragments, the geometry of acetylene, and the charges in the transition state for activated CC bond scission. It may be seen that as the binding energy of adsorbed acetylene increases with either anodic or cathodic charging of the surface, the stretch of the CC bond in order to reach the transition state decreases. This increases the σ–σ^* splitting on going in either direction, compared with its value on the uncharged surface. The orbital energy level diagram for acetylene in the transition state for CC bond scission is given in Figure 4. The σ_p^* mixing and stabilization increase on going cathodic and decrease on going anodic

Acetylene on Pt(111) and Fe(100)

J. Am. Chem. Soc., Vol. 107, No. 4, 1985 847

Table IV. Calculated CH Bond Activation Barrier (EA_{CH}), Stretch of the CH Bond (ΔCH), and Charges in the Transition State for Acetylene on the Δ Site of the Pt_7 Model of the Pt(111) Surface at Several Potentials

	potential, eV				
	−2	−1	0	+1	+2
EA_{CH}, eV	0.83	1.37	1.77	1.74	1.63
ΔCH, Å	0.30	0.40	0.45	0.45	0.40
C_2H_2 charge	−2.40	−1.65	−0.70	0.42	1.45
H charge	−0.18	−0.17	−0.13	−0.05	0.04

Table V. Calculated Binding Energy ($BE_{C_2H_2}$) of Acetylene, Height Above the Surface (h), CH Bending Angle Away from the Surface (θ), Carbon Bond Stretch (ΔCC), and Charges on Adsorbed Acetylene on the Fe_5 Model of the Fe(100) Surface at Several Potentials

	potential, V				
	−2	−1	0	+1	+2
$BE_{C_2H_2}$, eV		5.28	3.56	2.79	
h, Å		1.25	1.30	1.30	
θ, deg		65	65	65	
ΔCC, Å		0.40	0.36	0.34	
C_2H_2 charge		−2.05	−1.25	−0.39	
H charge		−0.05	−0.03	−0.02	

Figure 5. As in Figure 2 for CH bond scission transition state. Levels drawn heavy when 0.1 or greater occupation.

Figure 6. Acetylene plus Fe_5 energy level correlations for various d band positions (electrode potentials). Cross-hatched region contains 12 unpaired electrons.
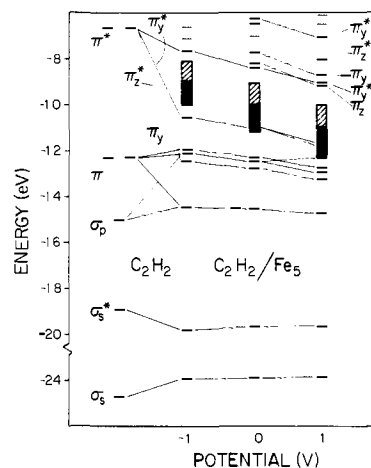
because of the shift of the d band.

We have also studied the potential dependence of CH bond activation of acetylene on the platinum surface. The activation barriers are calculated by bending one CH bond parallel to the surface (see Figure 1) and stretching it toward a platinum atom. When this is done, the angle of the other CH bond to the surface is found to be unchanged within 5°. The CH bond stretch and charges in the transition state are given in Table IV. At 0 V, the calculated activation barrier is 1.8 eV, and this decreases to 1.6 eV on the 21 atom cluster.[2a] Such values are close to, but several tenths of an electronvolt higher than, those deduced from recent thermal desorption studies.[8] This overestimate may result from the overestimate of the acetylenic CH bond strength, 6.9 eV, to be compared with the standard value of 4.2 eV. It should be mentioned that olefinic and aliphatic CH bond strengths in propylene are calculated in close agreement with experiment, and the activation barriers for these bonds on Pt(111) have been calculated to be less than 1 eV,[9] which agrees closely with thermal desorption studies.[8] The CH bond activation barriers also show the same trend as shown by the CC bond scission barriers and are slightly greater at neutral and cathodic potentials and much greater at anodic potentials. The orbital correlation diagram for acetylene in the transition state for the CH bond scission is shown in Figure 5, where it is seen that the CH σ^* orbital never mixes strongly with occupied metal band orbitals in the transition state. The activation of the CH bond in the cathodic direction is a result of increased donation to the leaving H atom and the CCH fragment. In the anodic direction, it is a result of increased donation from the σ bonding orbital involving a three-center metal–H–C bond as shown in Figure 5.

Results similar to those of acetylene on Pt(111) have been calculated for acetylene on Ni(100) at different potentials.[7g] The CC bond scission barrier is relatively high because of the smaller

spacial extent of the 3d orbitals on Ni compared to the 5d orbitals of Pt.

Adsorption and Dissociation of Acetylene on Fe(100) as a Function of d Band Position

The favored binding site for acetylene on the (100) surface of iron at various potentials is calculated to be the high coordination 4-fold site, where each carbon atom of acetylene bonds to two iron atoms. The calculated binding energy of acetylene on the 4-fold site, its geometry on adsorption, and the charges on the C_2H_2 and H species are tabulated in Table V for the potential range −1 to +1 V. As the potential increases on each side of this range, acetylene dissociates with the zero barrier. The binding energy of acetylene increases in the cathodic but decreases in the anodic direction, as compared to its value on the uncharged surface, and so does the equilibrium CC bond stretch. The CH bending angle away from the surface remains constant at 65° but the height decreases slightly in the cathodic direction. There is lot of charge transfer into the π^* orbitals of acetylene from the d band on going in the cathodic direction for the same reasons as outlined for the platinum surface in the previous section. The orbital energy correlation diagram for acetylene adsorbed on the Fe_5 model of iron(100) is in Figure 6.

On stretching the CC bond from the equilibrium value, it dissociates into CH fragments with small activation barriers, in the potential range −1 to +1 V, beyond which the fragmentation is downhill. The CH fragments thus formed are strongly adsorbed on the bridging sites with the carbon end down at a height about 1.2 Å above the surface. The binding energy of the CH fragments, the activation barriers to CC bond scission, the geometry of acetylene, the CC bond stretch from equilibrium value, and the charges in the transition state are given in Table VI. The onset of the increase in CH bond strength to the surface in the anodic direction requires a greater shift than that of platinum because the iron d band lies higher in energy.

Since the CC bond of adsorbed acetylene dissociates readily on the iron surface at all potentials, we now examine the CH bond

(8) Salmerón, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.

(9) Anderson, A. B.; Kang, D. B.; Kim, Y. *J. Am. Chem. Soc.* **1984**, *106*, 6597.

Table VI. Calculated CC Bond Activation Barrier (EA_{CC}), Binding Energy of CH Fragments[a] (BE_{CH}), Carbon Bond Stretch (ΔCC), CH Bending Angle Away from the Surface (θ), and Height Above the Surface (h) for Acetylene in the Transition State for CC Bond Activation at the 4-fold Site of the Fe_5 Model of the Fe(100) Surface at Several Potentials

	potential, V				
	−2	−1	0	+1	+2
EA_{CC}, eV	0.0	0.01	0.04	0.02	0.0
BE_{CH}, eV	9.50	5.97	3.88	3.17	3.75
ΔCC, Å		0.10	0.32	0.44	
θ, deg		70	75	80	
h, Å		1.25	1.25	1.25	
C_2H_2 charge		2.12	−1.43	−0.49	
H charge		−0.04	−0.03	−0.01	

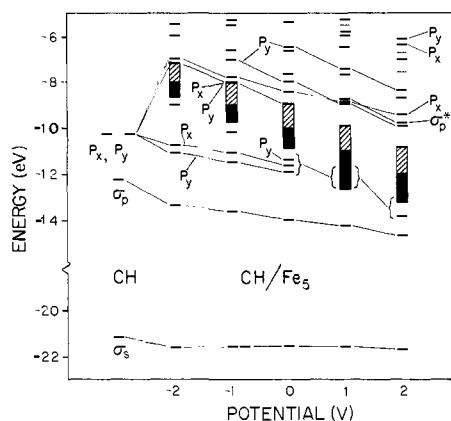[a]Relative to the energy of separated Fe_5 model and gas-phase acetylene.

Figure 7. As in Figure 6 for CH. Energy levels for orbitals with an occupation of 0.1 electron or more are drawn heavy.
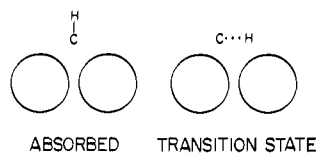

Figure 8. CH adsorbed and in transition state.

activation of the CH fragments as a function of potential. For this we consider the adsorption of one CH fragment on the bridging site of the Fe_5 model at various surface potentials. The orbital correlation diagram for CH adsorbed on the bridging site of the cluster is shown in Figure 7. When the CH bond is stretched after first making it parallel to the surface at a height 1.55 Å, it breaks into C and H atoms (Figure 8). The binding energy of CH at the bridging site, the CH bond activation barriers, the CH bond stretch, and charges on CH and H in the transition state are given in Table VII. As may be seen, for the −2-V surface potential, the CH bond breaks without a barrier but there is a slow decrease in the anodic direction beyond 1 V. The rapid decrease in the CH bond scission barrier in the cathodic direction is due to strong metal donation and participation of the CH σ^* orbital as shown in Figure 9. At anodic potential greater than 1 V, activation is the result of CH σ donation to the metal in a three-center bond as shown in Figure 9.

Discussion

The behavior of acetylene CC and CH bonds on platinum and iron is controlled by the increased metal-donating ability and accepting ability as the metal bands are shifted up and down, respectively. Our results suggest, in a perturbation sense, what will happen to adsorbed acetylene on metals to the left (cathodic) and to the right (anodic) of iron and platinum. As discussed in the Introduction section, such shifts may be viewed as a model for acetylene adsorbed on platinum and iron electrodes. It is probable that acetylene will displace adsorbed water from the

Table VII. Calculated Binding Energy of CH Fragment[a] (BE_{CH}), CH Bond Activation Barrier (EA_{CH}), CH Bond Stretch (ΔCH), and Charges on CH and H for CH in the Transition State on the Fe_5 Model of the Fe(100) Surface at Several Potentials

	potential, V				
	−2	−1	0	+1	+2
BE_{CH}, eV	8.38	6.61	5.57	5.27	5.68
EA_{CH}, eV	0.0	1.14	2.25	2.48	1.60
ΔCH, Å	0.30	0.35	0.35	0.40	0.25
CH charge	−2.83	−2.36	−1.52	−0.18	0.84
H charge	−0.16	−0.13	−0.06	−0.02	0.09

[a]Relative to the energy of separated Fe_5 model and CH fragment.
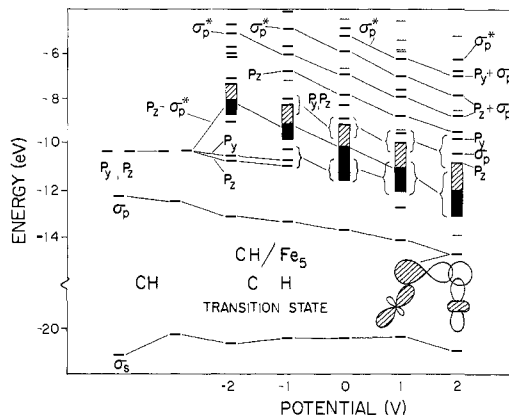

Figure 9. As in Figures 6 and 7 for CH bond scission transition state.

platinum electrode. Water is held to the metal by donation bonds,[10] as is acetylene, but acetylene adsorbs more strongly because of additional back-bonding from the metal to the π^* orbitals. Indeed, electrochemical studies have led to the conclusion that acetylene is adsorbed on a platinum electrode surface, displacing 2.1 water molecules per acetylene molecule, and that ionic adsorption from solution does not influence the electrochemistry of the adsorbed acetylene.[11] It has been found that at potentials 0.2 V and less (vs. the normal hydrogen electrode), acetylene is reduced to ethylene and ethane,[12] and at potentials greater than 0.35 V, it is oxidized to carbon dioxide with a current maximum at 1.18 V. Furthermore, adsorption of acetylene at the rest potential (0.25 V), with no current flowing, is associative, with the CC and CH bonds intact.[11] It is believed that the rate-limiting step in acetylene oxidation to CO_2 is the first deprotonation of adsorbed acetylene.[11] An activation energy of 1.8 eV has been determined for acetylene oxidation at the rest potential in acid solutions.[13] The rest potential should correspond approximately to 0 V on our scale. This value correlates well with our calculated CH scission barrier of 1.8 and 1.7 V at 0 and +1 V on our scale. As discussed in the Introduction section these barriers may be overestimated by several tenths of an electronvolt and so the experimental electrochemical value of 1.8 eV may reflect steric crowding. Though we calculate a CC scission barrier of 1.2 and 0.9 eV at these respective potentials, at saturation coverage, the barriers will be much higher due to crowding effects.[2a] It may also be noted that on going to a larger cluster, the CH and CC scission barriers at 0 V potential are slightly different, being 1.6 and 1.3 eV, respectively,[2a] and we expect nearly the same difference for other potentials as well. Once again, our arguments are qualitative ones based upon the numerical results of our calculations and the molecular orbital bonding analysis. In our calculations the adsorbed acetylene molecule is uncharged at a point between 0 and 1 V, and at 1 V in the CH scission transition

(10) Anderson, A. B. *Surf. Sci.* **1981**, *105*, 159.
(11) Delgado, A. B.; Castro Luna, A. M.; Triaca, W. E.; Arvia, A. J. *J. Electrochem. Soc.* **1982**, *129*, 1493.
(12) Davitt, H. J.; Albright, L. F. *J. Electrochem. Soc.* **1971**, *118*, 236.
(13) Johnson, J. W.; Wroblowa, H.; Bockris, J. O'M. *J. Electrochem. Soc.* **1964**, *111*, 863.

state, it bears a charge of +0.74. Thus it is probable that water molecules will coordinate and stabilize the leaving proton, as we have discussed for water adsorbed to the iron electrode,[7c] and this stability is responsible for the decrease in activation energy to 1 eV at potentials around 0.7–0.8 V in acidic solution.[13] In alkaline solutions, the activation barrier increases and the current increases.[13] The current increase has been associated with increased acetylene coverage,[13] possibly CCH_2 standing vertically, a phase seen in vacuum studies[4a] and studied theoretically.[2b] CH bond activation in such a species is less likely to be aided by direct interaction with the metal surface atoms, and this may be responsible for the increased barrier in alkaline solutions.

Our calculations show a low CH activation barrier in the cathodic direction, where reduction to ethylene and ethane is known to take place.[12] This implies a low barrier for hydrogenation of acetylene, which will happen when water is reduced, forming surface hydrogen atoms on the cathode surface. We have not studied this process here, but the reader is referred to our earlier study of water dissociation on Pt(111), which shows a barrier comparable to the CH activation barrier.[10]

To our knowledge, there are no published studies of acetylene reactions on iron electrodes for comparison with our theoretical results. In the anodic range 0.20–1.2 V, the surface is covered by the passive film, a hydrated oxide of 40-Å thickness,[14] which should prevent acetylene adsorption to iron metal. In the −0.45 to +0.20 V range, the iron electrode undergoes dissolution.[14,7d] If the surface has regions active to acetylene in this potential range, it appears from our results that acetylene should reduce to methane by hydrogenation of surface CH species. A small amount of methane was sometimes seen in the reduction of acetylene on platinum.[12] If the concentration of surface hydroxyl species is great enough, acetylene dissociation might be blocked, with the result that ethylene or ethane would be the reduction products.

(14) Frankenthal, R. P., Kruger, J. Ed. "Passivity of Metals"; Electrochemical Society: Princeton, NJ, 1978.

Aromatic Stability of Heterocyclic Conjugated Systems[†]

M. Randić,*[‡] N. Trinajstić,[§] J. V. Knop,[⊥] and Z. Jeričević[§]

Contribution from the Department of Mathematics and Computer Science, Drake University, Des Moines, Iowa 50311, Ames Laboratory,[∥] Iowa State University, Ames, Iowa 50011, Rugjer Boskovič Institute, 4100 Zagreb, Croatia, Yugoslavia, and the Computer Centre, University of Düsseldorf, 4000 Düsseldorf, Federal Republic of Germany. Received January 10, 1984

Abstract: The graph-theoretical approach for calculation of the aromatic stability of conjugated polycyclic hydrocarbons is extended here to polycyclic systems having a single heteroatom. Advantages of this algebraic approach, which yields *expressions* for the molecular resonance energies, are discussed. In particular, the relative stabilities of *positional* isomers have been predicted for many derivatives of benzenoid conjugated systems in which a carbon atom is replaced by a heteroatom. The basis for the analysis is conjugated circuits (circuits defined within individual Kekulé valence structures) and their enumeration. The results are illustrated on azabenzenoid systems (N-arenes), but the nonnumerical conclusions are valid for a broader class of heterocyclic compounds.

One of the first questions to be considered when one proposes the synthesis of a novel compound is its stability, or its intrinsic capability of not easily decomposing. For conjugated systems, molecular resonance energy (RE) is a parameter that gives a useful measure of this intrinsic stability. RE is defined as that part of the molecular binding energy which is not accounted for by bond additivity, which in the case of acyclic systems suffices to represent the molecular energy. This extra stability bequeathed on some polycyclic conjugated systems is associated with the "aromatic" character of the compounds, and one speaks of *aromatic stability* of polycyclic conjugated systems or heterocyclic conjugated systems. There are two fundamentally different approaches to the study of molecular resonance energy and aromaticity: (a) use of quantum chemical computations that will produce a *numerical value* for RE and (b) use of graph-theoretical enumerations that give *algebraic expressions* for RE. The former will yield absolute values for RE of molecules of interest; the latter offers an insight on relative values, even without a knowledge of precise individual magnitudes. Observe the profound difference of the two kinds

of results. In view of the complexity of rigorous computations on polycyclic conjugated hydrocarbons, not to mention heterocyclic conjugated systems of similar size, the choice is not between quantitative calculations of reliable accuracy and qualitative predictions of simple or apparently simplistic schemes that may properly account for some aspects of the bonding. What is needed is a scheme that, even if not comprehensive, can correctly answer some of the questions of interest. As will be argued here a graph-theoretical approach based on the concept of conjugated circuits[1] (vide infra) offers a theoretical model capable of answering some questions on molecular structure with utmost reliability. In order to illuminate the profound difference between quantum chemical calculations (such as SCF MO methods applicable to polycyclic conjugated hydrocarbons) and algebraic considerations of graph theory, let us consider the question, "which has greater aromatic stability, anthracene or phenanthrene?" There is no way to answer this question a priori within the quantum chemical domain. To find the answer, one has to perform the necessary calculations, obtain the relevant numerical data, and a posteriori deduce the answer. Through the use of a graph-theoretical concept of conjugated circuits, one can derive expressions for RE. These expressions, when combined with the very plausible assumption that smaller conjugated circuits (benzene *is* an illustration!) have larger RE than larger conjugated circuits,

(1) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68.