

## COMMUNICATIONS TO THE EDITOR

## Dependence of Chemisorbed Hydrocarbon Bond Activation on the Metal d Orbital Size

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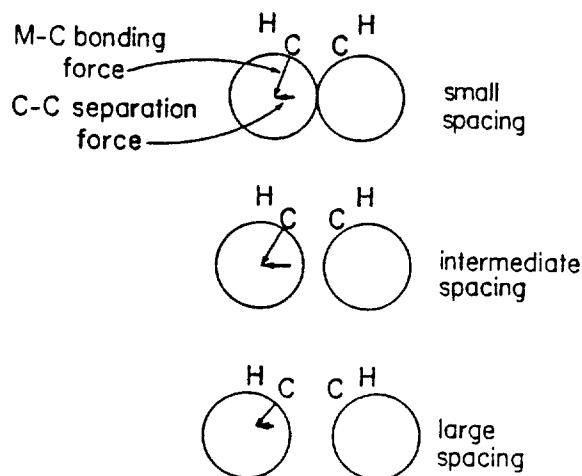
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The adsorption of acetylene and ethylene has been studied using various experimental techniques on many metals which are located in the central and right-hand regions of the transition series. Adsorption studies of unsaturated hydrocarbon molecules on metals from the left-hand region have been rare. These metals form very stable oxides and carbides which render high-purity surfaces difficult to prepare. Once prepared, these surfaces might be expected to show high activity toward the decomposition of unsaturated hydrocarbons.

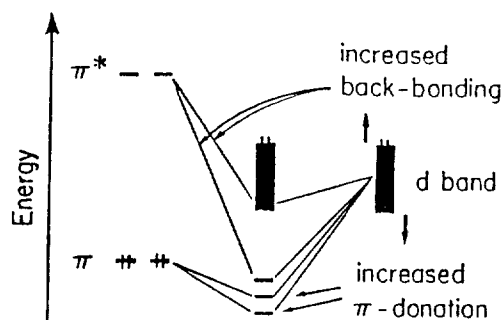
The purpose of the present study is to establish variations and trends in structures and reactivity and molecular orbital interpretations for many metals, particularly at the left of the transition metal series which have not yet been studied experimentally or theoretically in this context. The results will be fully analyzed in terms of metal atom properties and molecular orbital bonding theory.

There are several physical variables to consider in predicting or explaining the reactivity of a transition metal surface toward acetylene. They are atomic surface structure, d band position, d band electronic occupation and atomic d orbital size.

Several of these variables have already been explored in recent studies. It has been found that those surfaces of Pt<sup>1</sup> and Fe<sup>2</sup> which have either large or small metal atom spacing are less active toward C≡C bond scission than those with intermediate spacings. This is because of the forces on the C≡C bond due to C-M bond formation as illustrated schematically in Figure 1. On these metals the energy position of the d band has been found to influence C≡C bond activation. The occupied s + d band orbital energy levels of Pt and Fe are straddled by the empty π\* and occupied π energy levels of acetylene, as shown in Figure 2. Moving the metal band up (which corresponds to cathodic charging of an electrode surface in a dielectric medium) increases metal electron donation to the acetylene π\* orbitals, leading to C≡C bond scission.<sup>3</sup> Moving the metal band down (corresponding to anodic charging) increases acetylene π donation to the metal, reducing the C≡C bond order and also leading to scission.<sup>3</sup> It has been noted<sup>3</sup> that d electron count may be relatively unimportant to C≡C bond activation because the antibonding counterparts to π donation and back bonding to π\* orbitals are



**Figure 1.** Schematic representation of C≡C bond scission forces due to M-C bond formation forces for different metal surface atom spacings.



**Figure 2.** Schematic picture showing position of occupied transition metal valence d band relative to acetylene π and π\* orbital energy levels and the effects of band shifts.

above the occupied metal band and always empty while the bonding combinations are at the bottom and always occupied, as may be seen in Figure 3. By way of contrast, d electron count is important to the structure of adsorbed CO because the antibonding counterparts of the CO π donation bonds lie within the d band<sup>4</sup>.

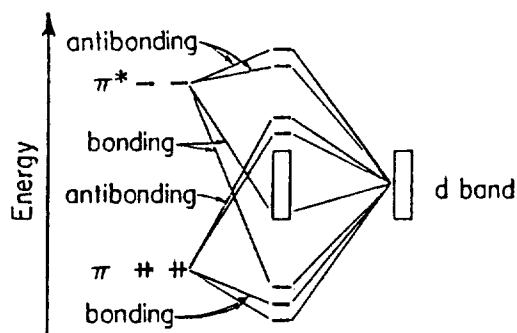


Figure 3. Representative correlation diagram for acetylene chemisorption on a transition metal surface.

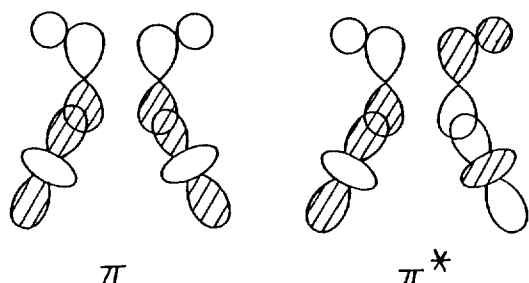


Figure 4. Bonding orbitals for acetylene in a di- $\sigma$  site as derived from acetylene  $\pi$  and  $\pi^*$  orbitals.

Finally, there is the d orbital size which is the topic of this work. Years ago, Anderson found that the difference in reactivity between iron and nickel surfaces toward acetylene could be explained in terms of a single atomic property, the size of the valence 3d orbital.<sup>5</sup> The property examined was the barrier to the carbon triple bond scission energy. It was known from experimental<sup>6</sup> and theoretical<sup>2,7</sup> studies that the barrier on Fe (100) surface is small, allowing dissociation to CH fragments at temperatures as low as 123K. On a Ni (111) surface, acetylene adsorbs stably in a triangular site with carbon bond scission barrier of more than 1eV (about 1.1eV) according to the calculations.<sup>5</sup> This is consistent with the fact that acetylene is stable at temperature up to 470K in the (2  $\times$  2) coverage.<sup>8</sup>

We find that by using Fe<sup>+1</sup> d orbitals, which are nearly the same as Ni<sup>0</sup> orbitals, acetylene is stable on Fe (100) with a barrier similar to that found for the Ni (111) surface. The bonding of acetylene to a metal surface is largely a result of  $\pi$ -d bonding and  $\pi^*$ -d back-bonding stabilizations as in Fig. 4. The back-bonding interaction is a classic effect and no doubt contributes to weakening and lengthening the acetylene carbon bond. The smallness of the d orbitals in Ni can be mentioned as the reason for the higher barrier for acetylene C $\equiv$ C bond scission on Ni (111) compared to Fe (110). Our theoretical study of acetylene chemisorption on small cluster models of (100), (110) and (111) surfaces of vanadium shows acetylene should adsorb dissociatively on these surfaces even at low temperature because the calculated barrier are very small or close to zero. There is a strong temptation to correlate the increased vanadium d orbital size compared with iron and nickel to the enhanced reactivity in terms of the overlap of metal d orbitals with carbon s and p and hydrogen s orbitals, particularly since the d band positions are all in a common energy range and d orbital occupation is not a major influence.

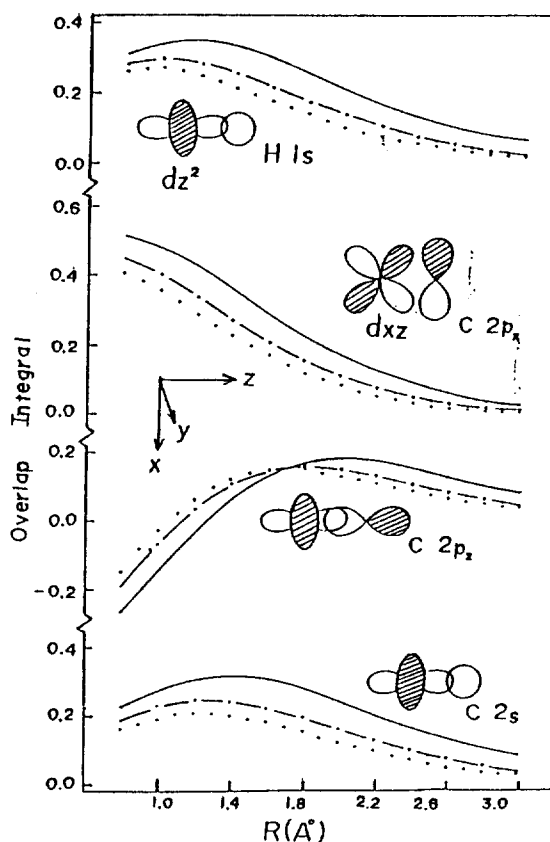


Figure 5. Variation of overlap integrals against the metal-carbon and metal-hydrogen bonding distance (— V, --- Fe, ... Ni).

Table 1. Extended Hückel Parameters

Orbitals	$\zeta_1$	$C_1^a$	$\zeta_2$	$C_2^a$
V	4s	1.20		
	4p	0.75		
	3d	4.75	0.456	1.50
Fe	4s	1.575		
	4p	0.975		
	3d	5.35	0.5366	1.80
Ni	4s	1.825		
	4p	1.125		
	3d	5.75	0.5683	2.00
C	2s	1.625		
	2p	1.625		
H	1s	1.30		

<sup>a</sup>Coefficients used in double- $\zeta$  expansion.

The effects of the decreasing d orbital Slater exponents and consequent increasing orbital size on going left show that the vanadium 3d orbitals are more diffuse than the iron and nickel 3d orbitals. Overlap integrals ( $M 3d_{z^2}|C 2s$ ), ( $M 3d_{z^2}|C 2p_z$ ), and ( $M 3d_{xz}|C 2p_x$ ) in Figure 5 are indeed larger for vanadium with the respective calculated values of 0.25, 0.18, and 0.18 at typical metal-carbon distances of around 2 Å, indicating the  $\pi$  and  $\pi^*$  stabilization are greater for acetylene on the vanadium surfaces than on iron and nickel surfaces. This leads to strong metal-carbon bonding and weakened C $\equiv$ C bonding. Figure 5 also shows the overlap integral ( $M 3d_{z^2}|H 1s$ ) is larger for vanadium with the calculated value of

0.22, which is responsible for the very low C-H bond scission barrier. Finally, we consider the overlap of carbon s and p orbitals with metal s and p orbitals. At bonding distances ( $M\ 4s|C\ 2p$ ) is somewhat smaller for vanadium and ( $M\ 4s|C\ 2s$ ) is somewhat greater for vanadium. These small differences are barely distinguishable on the graphical scale of Figure 5 and are not significant. The metal p orbitals are far removed in energy from carbon levels and should play an even smaller role determining surface reactivity than the metal s orbitals. For these reasons the difference in reactivity between vanadium, iron, and nickel might be expected to be attributed to d orbital size alone. The extended Hückel method<sup>9</sup> was used in all calculations. The parameters are listed in Table 1.

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## Molecular Orbital Studies on the Catalytic Properties of $\text{MoO}_3$ toward Propylene Oxidation

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$\text{MoO}_3$  can catalytically convert propylene into acrolein through the selective oxidation and may be used as a model to understand the catalytic properties of  $\alpha$ -bismuth molybdates.<sup>1</sup> To probe the electronic implications of propylene adsorption on  $\text{MoO}_3$ , atom superposition and electron delocalization-molecular orbital (ASED-MO) calculations are carried out on both naked  $\text{MoO}_3$  and the whole surface/adsorbate system.

In the ASED-MO theory<sup>3</sup> the electronic charge density of a molecule is partitioned into free atom parts and an electron delocalization bond formation component. As the atoms come together to form a molecule, the electrostatic forces on the nuclei are integrated to yield a repulsive energy due to rigid-atom densities and an attractive energy due to electron delocalization. The sum is the exact molecular binding energy. The atom superposition energy is easily calculated and the electron delocalization energy, though not directly calculable, is well approximated by one-electron molecular orbital energy obtained by using a hamiltonian which shares some features with the extended Hückel hamiltonian. Theory parameters used in the calculations for Mo and O come from an earlier study<sup>4</sup> of the electronic properties of crystalline  $\text{MoO}_3$  by Anderson. For C, the respective 2s and 2p orbital exponents and ionization potentials are 1.658au, 18eV, and 1.618 au, 9.26eV; or H, the 1s parameters are 1.2au and 11.6eV.

In molybdate,  $\text{MoO}_3$ , the  $d^0\ \text{Mo}^{\text{VI}}$  cations are surrounded by six oxygen anions in a distorted octahedral arrangement with varying Mo-O bond lengths from 1.84 to 2.34 Å.<sup>5</sup> Calculations on a  $\text{MoO}_6^{6-}$  cluster model from the crystal produce the energy level structure in Fig. 1. The MoO bonding

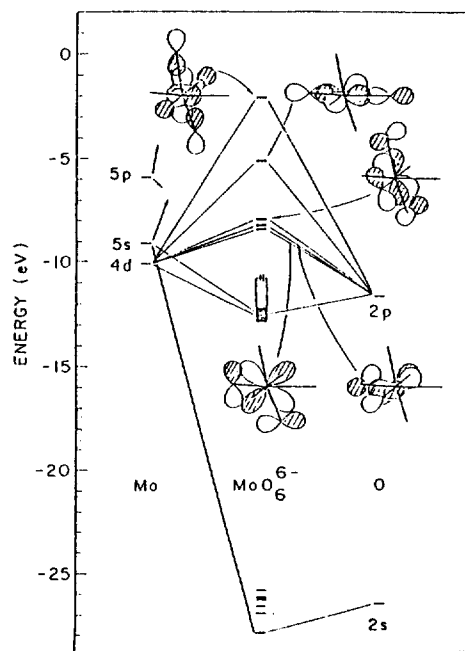


Figure 1. Correlation diagram and molecular orbitals for a  $\text{MoO}_6^{6-}$  model of  $\text{MoO}_3$

levels are oxygen in character. The O 2p band is filled and the Mo 4d band is empty because molybdenum is present as  $\text{Mo}^{\text{VI}}$ . The empty lower slightly split "t" and more widely split upper "e" levels are a result of distortion in the lattice away from perfect octahedral symmetry. Quantum mec-