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# Activation of C-H Bonds by Metals and Metal Oxides

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Extensive atom superposition and electron delocalization molecular orbital(ASED-MO) calculations of CH bond scission mechanisms and transition state structures on various metal and metal oxide surfaces have recently uncovered the bonding interactions governing CH activations on these surfaces. We have examined CH bond cleavage in adsorbed unsaturated molecules on iron,[1,2] platinum,[2-5] vanadium[6], and α-bismuth molybdate($Bi_2Mo_3O_{12}$).[7] We have also examined the dehydrogenation of methane on iron[8] and methoxy coordinated to molybdenum trioxide.[9] The molecular orbital explanations of CH activation in all these cases show common features. In each case, the transition state is reached with a stretch of 0.4-0.6 Å in the CH bond toward the metal atom or oxygen anion which accepts the hydrogen atom. In the transition state the CH bond is significantly stabilized by forming σ-donation bond to the acceptor(A). The degree of CH activation depends on what happens to the two electrons in the CH-M or $CH-O^{2-}$ antibonding counterpart σ^* orbital. There are four possibilities: (a) the CH-A σ^* orbital remains occupied in the transition state, in which case the barrier is high; (b) the CH-A σ^* orbital loses one electron by photoexcitation, in which case the barrier is low; (c) the CH-A σ^* orbital is stabilized by a higher-lying empty orbital, in which case the barrier is low; (d) the CH-A σ^* orbital donates one or both electrons into low-lying acceptor orbitals, in which case the barrier is low. Case(a) is envisioned in orbital correlation diagram(see Figure 1) which explains the high bond scission barrier. Case(b), (c), and(d) are illustrated in Figure 2. The first three cases are exemplified by making some general comments on optimizing the conditions for CH activation in methane and other alkanes. The last one is treated for the CH bond activations on Fe(100) and V(100) surfaces in the present study.

Case(a): Methoxy on MoO_3[9] Molybdenum trioxide has a filled O^{2-} 2p band which is is ~3 eV beneath the bottom of the empty Mo^{VI} 4d band.[10] When surface-coordinated methoxy, OCH_3, is oriented for H transfer to a surface O^{2-} and the transition state is variationally optimized, the $CH-O^{2-}$ σ^* orbital is found in the band gap and it is doubly occupied. The calculated activation barrier is therefore high(2.6 eV), which is reflected by the 500 °C temperature required for reaction. This is a case of limited or non-activation since the $CH-O^{2-}$ σ donation orbital and $CH-O^{2-}$ σ^* orbital are both
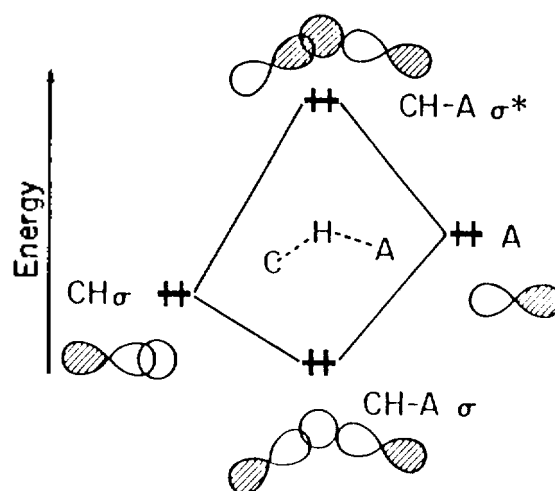

Figure 1. Schematic representation of the closed-shell repulsive interactions which afford a high activation barrier to CH bond cleavage by H acceptor.
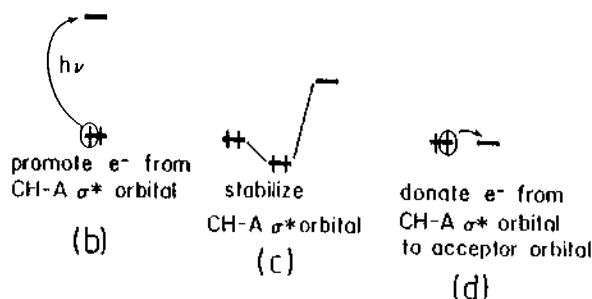
Figure 2. Various cases of CH bond activation.

doubly occupied and the resulting transition state C-H-O bond order is zero.

Case(b): Photoactivation of Methoxy on MoO_3[9] Referring to Case(a) above, an O 2p→Mo 4d charge transfer excitation creates a hole at the top of the O 2p band. Now as the CH bond is stretched toward the transition state the $CH-O^{2-}$ σ^* orbital energy level runs up through the O 2p band and picks up the hole. In the transition state this orbital is again in the band gap but is only half-occupied. The transition state
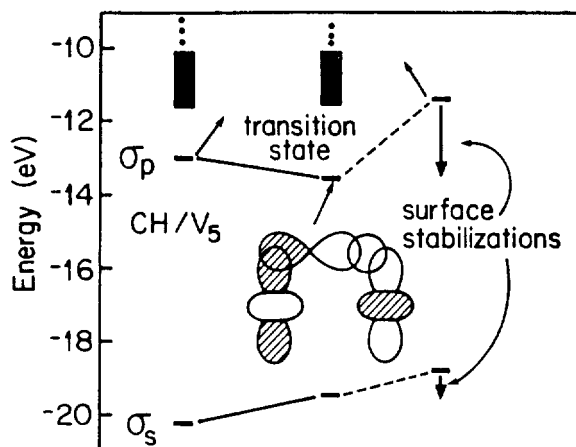
Figure 3. CH σ donation stabilization in the transition state for the CH bond cleavage on V_5 model.

bond order is one half and the barrier is cut by nearly half, which is qualitatively consistent with experimental studies showing reaction at ambient temperatures in the presence of mercury light.[11]

Case(c): Propylene on α-Bismuth Molybdate[7]. Propylene coordinates by a π donation bond to an unsaturated Mo^{VI} center at the oxide surface. A methyl hydrogen may be stretched to a transition state for donation to a surface O^{2-} The $CH-O^{2-}\sigma^*$ transition state orbital energy level lies above the O 2p band but is stabilized by mixing with the higher-lying π^* orbital of the olefinic end. The transition state bond order is formally zero as the $CH-O^{2-}$ σ^* orbital remains doubly occupied, but due to this stabilization the activation energy is calculated to be only 1.1eV (compared to 0.8-0.9 eV from experimental estimates[12]).

Case(d): CH Bond Activations on Fe(100) and V(100) surfaces We first consider the bond scission of diatomic CH on the bridging site of the Fe(100) surface. When the CH bond is stretched after first making it paralled to the surface at a height 1.55 Å, it breaks into C and H atoms with a low barrier of 1.14 eV.

The calculated binding energy for CH to Fe_5 is 6.0 eV in the bridging position when the free CH calculated distance of 1.15 Å is used. To place CH in the bridging position parallel to the surface at the lowest energy, 1.55 Å above the surface, costs 1.0 eV. On stretching, a 0.14 eV barrier is reached at about 1.55 Å, with CH raised slightly to 1.65 Å high.

The activation barrier for CH bond breaking in CH species on the bridging site of the V_5 cluster is calculated to be 0.7 eV. About 90% of the total barrier comes from tilting the CH parallel to the surface. The transition state occurs with the CH bond parallel to the surface and stretched 0.4 Å. As

the CH bond stretches toward the transition state, the CH-metal σ^* orbital energy level rises through the filled metal band and reaches a position above it in the transition state. In doing so it donates its two electrons to metal acceptor orbitals at the Fermi level. The barrier for stretching the CH bond is low because of the stabilization due to the CH σ donation to the metal in a three-center bond as shown in Figure 3.

The key to activating CH bonds in heterogeneous systems is the stabilization or emptying of an occupied three-centered CH-A antibonding orbital in the transition state. This orbital is antibonding between the CH σ orbital and an orbital on the acceptor atom(A). The low-lying CH-A bonding counterpart orbital is occupied and stabilized as a three-centered σ bond. Enhanced activation may be achieved on metal oxides by photon induced charge transfer excitations or by cathodic and anodic shifts of metal valence bands by increased donation into the CH σ^* orbital in the former case and increased CH-metal σ stabilization activation on vanadium surface because of the large overlap with the H 1s orbital.

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