Generalized Valence Bond Studies of the Electronic States of $NiCH_2$ and $NiCH_3$

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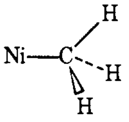
Abstract: Generalized valence bond and configuration interaction calculations were carried out for $NiCH_2$ and $NiCH_3$. In both cases the lower states have the character of Ni $(4s^1 3d^9)$ with the Ni 4s orbital bonding to the singly occupied $C\sigma$ orbital. The geometries were optimized, leading to NiC = 1.78 Å for $NiCH_2$ and NiC = 1.87 Å for $NiCH_3$. The calculated bond energies are $D(Ni\text{-}CH_3)$ = 60 kcal and $D(Ni\text{-}CH_2)$ = 65 kcal, with a weak π bond in the latter case.

Although metal-carbon bonds play an important role in both homogeneous and heterogeneous catalysis of hydrocarbons,[2] little is known about the precise character of such bonds from either experimental or theoretical viewpoints.[3] As a first step in studying such systems theoretically, we have examined the bonding of CH_3 and CH_2 to a single Ni atom.



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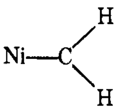

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Hartree-Fock (HF), generalized valence bond[4] (GVB), and configuration interaction (CI) calculations were carried out using a basis set of double zeta quality[5] (and including d functions on the carbon). All calculations are ab initio except that a modified effective potential[6,7] is used to replace the argon core of the Ni (reducing Ni to a ten-electron atom).

For $NiCH_2$, Ni-C bond lengths from R = 1.60 Å to $R = \infty$ were considered and HCH bond angles were optimized near the optimum R. The CH bond lengths were optimized near the optimum R and HCH angles. For $NiCH_3$ the CH bond length was fixed at 1.098 Å (a typical CH bond length for a methyl group and the optimum value calculated for $NiCH_2$) and the Ni-C bond length and the NiCH bond angle were fully optimized. In the GVB calculations we correlated all Ni-C and C-H bonds, leading to GVB(4) for both $NiCH_2$ $(^1A_1)$ and $NiCH_3$. Similar calculations were carried out for all relevant excited states.

In the CI calculations we included the optimum GVB orbitals for the Ni-C bonds plus two sets of Ni d orbitals (obtained from the various states). The CI included all the GVB correlations; in addition, for each state all single excitations into the virtual space were allowed. The result was 328 to 1030 spin eigenfunctions (380 to 3792 determinants) for $NiCH_2$ and 128 to 530 spin eigenfunctions (152 to 999 determinants) for $NiCH_3$.

Consider first the bonding of Ni to CH_3. In order to understand the character of these states recall that there are two low-lying states of Ni: $^3F(4s^2 3d^8)$ and $^3D(4s^1 3d^9)$ separated by 1 kcal. We find that for Ni the 4s orbital is ~2.5 times the size of the 3d orbital, and hence the interaction of Ni 4s with $C\sigma$ (the nonbonding singly-occupied sp^3-like orbital of CH_3 radical) dominates the bonding. The interaction of $C\sigma$ with $(4s)^1(3d)^9$ is quite attractive (bonding of $C\sigma$ and 4s), while the interaction of $C\sigma$ with $(4s)^2(3d)^8$ is repulsive (Pauli repulsion of $(4s)^2$ and $C\sigma$) at large R and only moderately attractive for small R. Given that Ni has the overall character of $4s^1 3d^9$ leads to five configurations of $NiCH_3$ depending upon which of the five d orbitals is singly occupied (or equivalently which has the hole). These states will be denoted as

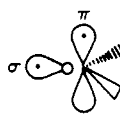
$$d\delta^+ = x^2 - y^2, \quad d\delta^- = xy, \quad d\pi^+ = yz, \quad d\pi^- = xz,$$
$$d\sigma = 2z^2 - x^2 - y^2,$$

where the σ, π, δ indicate the symmetry with respect to the Ni C axis and the + or − indicate the symmetry with respect to a particular NiCH molecular plane.

Just as in NiH[7] and NiCO[8] we find that the best state has the hole in a δ orbital ($d\delta^+$ or $d\delta^-$) with the $d\pi^\pm$ state 9.0 kcal higher and the $d\sigma$ state 9.8 kcal higher. The optimum geometry for the ground state is R_{NiC} = 1.87 Å and ∠NiCH = 109.4° and the calculated bond energy is 60 kcal. The bond energies of these various states are given in Figure 1. The total charge transfer from the Ni to CH_3 is 0.42 electrons (based on Mulliken populations). The two GVB orbitals of the $NiC\sigma$ bond have an overlap of S = 0.751 and hybridizations of Ni $4s^1 4p^{0.014} 3d^{0.32}$ and C $2s^1 2p^{2.93} 3d^{0.024}$.

The NiC bond length (1.87 Å) is slightly shorter than the 1.90 Å calculated[8] for NiCO, but slightly longer than the 1.82 Å found experimentally[9] for $Ni(CO)_4$. The calculated bond energy is at the upper limit of the 40-60 kcal often estimated for alkane-transition metal bonds;[10] however, no firm experimental values are known.[11]

As a basis for describing the bonding in $NiCH_2$ we will now examine the CH_2 fragment. The ground state of CH_2, $^3B_1$ $(\sigma\pi)$ has singly occupied a single electron in each of two nonbonding orbitals, denoted as $C\sigma$ and $C\pi$ as in **3** leading to an HCH bond angle of 135°,[12] while the first excited state $^1A_1$ (σ^2) (at 0.88 eV)[13] can be viewed as having two electrons in the $C\sigma$ orbital as in **4** leading to an HCH angle of 102.4°.[14]



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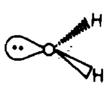

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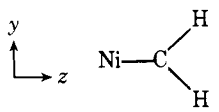
We find that the lower states of $NiCH_2$ are analogous to those of $NiCH_3$ with the Ni having the character $^3D(4s^1 3d^9)$ and the CH_2 fragment of $NiCH_2$ having the character **3** of the $\sigma\pi$ state. The interactions between the $C\pi$ orbital and the Ni d orbitals is weak and hence we end up with ten low-lying states, a singlet and triplet for each of the five locations of the d hole on the Ni (the $C\pi$ orbital being singlet or triplet paired with the singly occupied d orbital).

Taking the coordinate system as



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we find the states of $NiCH_2$ to be very similar to those of $NiCH_3$ *except* for the $d\pi^-$ (d_{xz}) states. Thus the $d\delta^-$ state

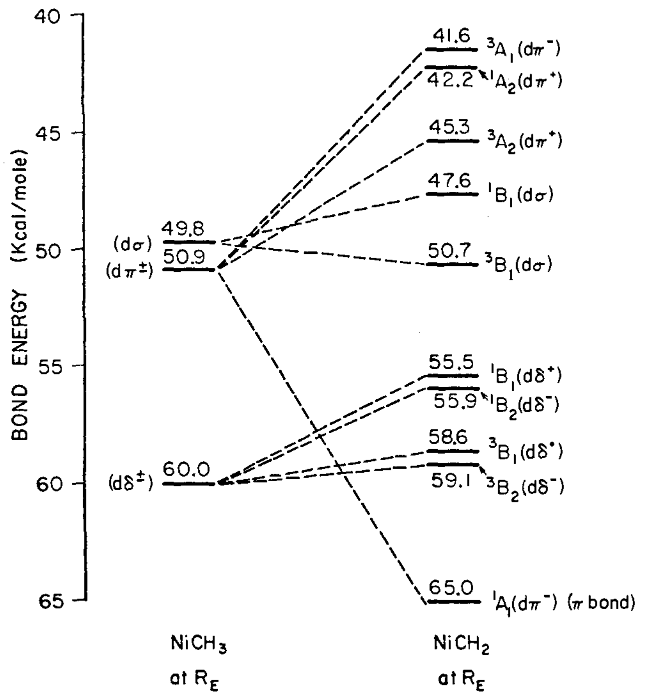


Figure 1. The bond energies D_e(Ni-CH$_n$), in kcal/mol, for the lower states of $NiCH_3$ and $NiCH_2$. In each case the geometry for the ground state is used (e.g., the D_e for $NiCH_2[^3B_2(d\delta^-)]$ is 62 kcal rather than the 59 kcal in the figure).

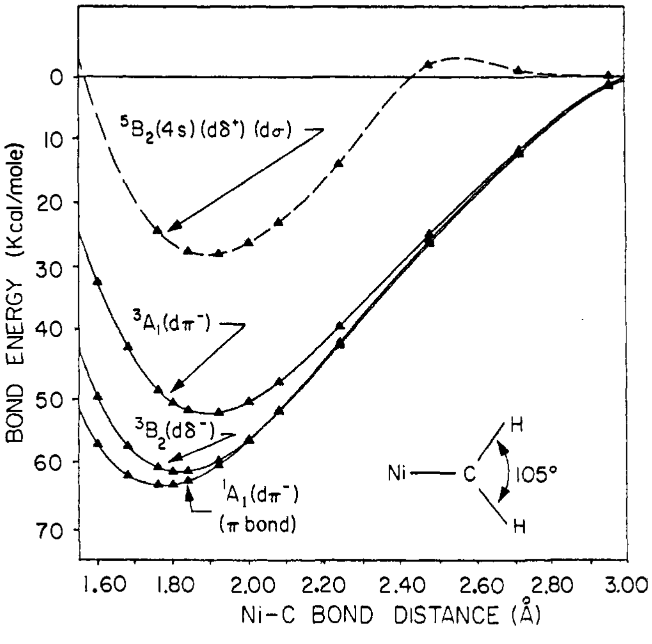
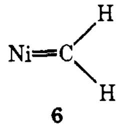


Figure 2. The potential energy curves for several states of $NiCH_2$. Here the HCH bond angle is taken as 105°.

leads to a bond length of 1.84 Å (the optimum HCH bond angle is 120°) and a bond energy of 62 kcal, while excitation energies to the $d\delta^-$, $d\pi^+$, and $d\sigma$ states are similar to those of $NiCH_3$ as shown in Figure 1. As was expected, the $d\pi^-$ (d_{xz}) state is different since the $d\pi^-$ orbital overlaps the singly occupied π orbital of CH_2. As a result, the singlet state gets extra bonding and one might represent this state as



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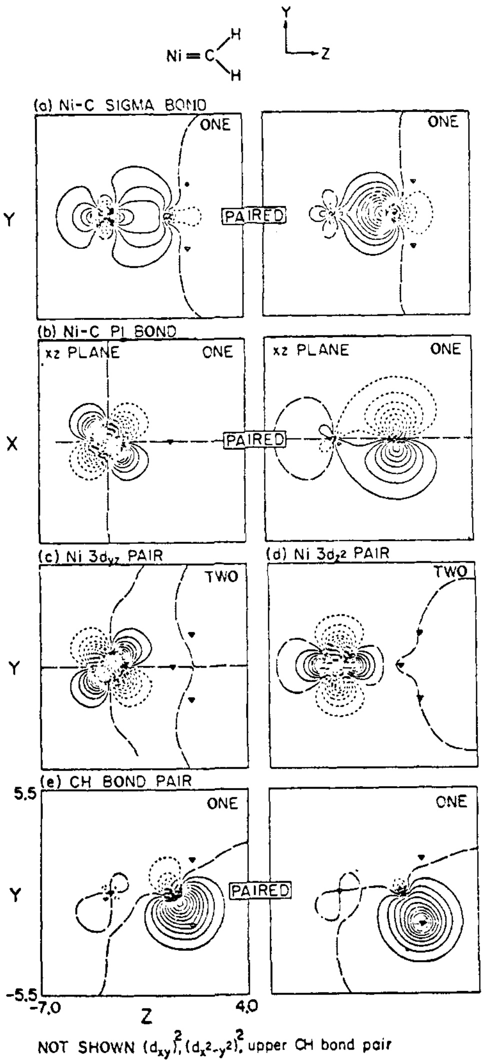
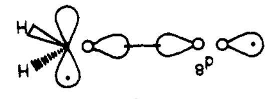


Figure 3. The GVB orbitals for the $^1A_1$ (π^-) ground state of $NiCH_2$ (R_{CH} = 1.071 Å, R_{NiC} = 1.76 Å, angle HCH = 110°). The long dashes indicate zero amplitude. All contours are separated by 0.05 au. The nuclei are indicated by triangles.

(Concomitantly, the triplet state gets extra antibonding.) However, because the Ni d orbitals are so much smaller than the bond orbital, the Ni $d\pi^-$, Cπ overlap is quite small (S = 0.076 for the atomic orbitals) and the extra π bonding is quite small. As a result, the singlet $d\pi^-$ state ($^1A_1$) leads to a bond energy of 65 kcal, a NiC bond length of 1.78 Å, and an HCH bond angle of 113.7°. Thus the state **6** with a π bond is only 3 kcal lower than the δ state without it. The corresponding $d\pi^-$ triplet state ($^3A_1$) is 23 kcal higher (at R_e); thus we can consider the singlet $d\pi^-$ state to have ~12 kcal of π bonding (and the triplet state ~12 kcal of π antibonding). The reason why the π-bonded state is only 3 kcal below the δ state is that a state with a $d\pi$ hole is intrinsically 9 kcal higher than a state with a $d\delta$ hole (as found for $NiCH_3$).

The potential curves for the $^{3,1}A_1$ ($d\pi^-$) and $^3A_2$ ($d\delta^-$) state are shown in Figure 2 along with one of the states that arises from bonding CH_2 to a $4s^23d^8$ configuration of Ni. At small R the bonding in this higher state can be visualized as



with two 4s4p hybrids each with one electron, one bonding to the CH_2 and one pointing the opposite direction.

The optimum GVB orbitals of the $NiCH_2$ ground state (singlet $d\pi^-$ or $^1A_1$) are shown in Figure 3. The two orbitals of the σ bond are given in Figure 3a (these orbitals have an overlap of 0.79, typical of a σ bond). As the bond is dissociated, the left orbital becomes Ni 4s while the right orbital becomes $\sigma(CH_2)$. At R_e the hybridization of these orbitals is Ni $4s^1 4p^{0.034} 3d^{0.25}$ and C $2s^1 2p^{1.52} 3d^{0.014}$, respectively. The orbitals of the π bond are shown in Figure 3b (they have an overlap of 0.25). Here the hybridizations are Ni $3d^1 4p^{0.0002}$ and C $2p^1 3d^{0.0005}$, respectively. The self-consistent Ni dσ and $d\pi^+$ orbitals are shown in Figure 3cd; they interact only weakly with the CH_2 group. The $d\delta^+$ and $d\delta^-$ orbitals are quite atomic-like and are not shown. THE CH bond pairs (only one is shown) are quite similar to the CH bond pairs of CH_2 (the carbon hybridization is $2s^1 2p^{1.88} 3d^{0.0069}$).

The total charge transfer from Ni to CH_2 is 0.56 electrons for $^1A_1$ ($d\pi^-$) and 0.51 electrons for $^3A_2$ ($d\delta^+$)(both based on Mulliken populations).

Because of the small overlap of the two orbitals in the π bond, HF calculations do extremely badly for the $^1A_1$ ($d\pi^-$) state. Consequently HF leads to a $^3A_2$ ($d\delta^+$) ground state and puts the correct ground state, $^1A_1$, 3.8 eV higher. Clearly, HF is not adequate for studying transition metal-carbene systems.

In summary we find that $Ni{=}CH_2$ and $Ni{-}CH_3$ lead to bond energies of 65 and 60 kcal, bond lengths of 1.78 and 1.87 Å, and NiCH bond angles of 123.5° and 109.4°, respectively. In both cases the bonding is basically that of an Ni 4s orbital and a carbon lobe orbital with only a small contribution due to π bonding in $NiCH_2$. Although the numbers are consistent with general ideas about metal-carbon bonds, there is little information with which to compare experimentally.[15]

References and Notes

(1) (a) Partially supported by a grant (DMR7-04965) from the National Science Foundation and by a grant (PRF-7683-AC6) from the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Presented at the W. F. Libby Symposium and Workshop on the Relation between Science and Technology in Heterogeneous Catalysis. University of California, Los Angeles. March 18–19. 1976.

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(15) Recently Hartree–Fock calculations have been carried out on $MnCH_2$ (B. R. Brooks and H. F. Schaefer III, unpublished). They find a MnC bond length of 2.16 Å and a bond strength of 33 kcal; these values are long and small, respectively, possibly because of the lack of electron correlation effects.

Localized Molecular Orbitals for Cumulenes. Three-Center Bonds, Fractional Bonds, and Bending Force Constants

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Abstract: PRDDO wave functions were localized using the criterion of Boys for C_nO_2 (n = 1, 3, 5, 7), C_n (n = 3, 5, 7), H_2C_nO (n = 1, 2, 4, 6), and $H_2C_nH_2$ (n = 2, 3, 5, 7). Ab initio wave functions were localized using the criterion of Edmiston and Ruedenberg for C_3 and ketene. The two localization criteria produced nearly identical results for C_3, but different results for ketene, the principal difference being the representation of the CO linkage. Three-center CCC bonds rather than cumulated double bonds are found in C_nO_2 and C_n molecules. Cumulated double bonds were found in H_2C_nO and the $H_2C_nH_2$ molecules. In C_nO_2, H_2C_nO, and C_n ($n > 3$) fractional bonds to carbon (inherently delocalized LMO's) are found. The localized molecular orbitals (LMO's) fall into simple patterns, most easily understood if the σ and π orbitals are localized separately. Both CCC bending and CH_2 out-of-plane bending are discussed and interpreted in the context of localized orbitals. Bond indices, valencies, and atomic charges are also reported. Soft bending potentials are associated with three-center CCC bonds and with significant negative atomic charges. High bending force constants are associated with fractionally bonded carbons and positive atomic charges.

The structure of carbon suboxide, an oxycumulene, has been a subject of both experimental and theoretical interest for over 40 years. Both linear and bent structures have been proposed.[1-7] The anharmonic nature of the CCC bending potential is now accepted as the correct explanation for the anomalies in the spectra of carbon suboxide.[2,3,7-11] A double-minimum potential favoring a CCC angle of ca. 160° and having a barrier to the linear configuration less than the lowest vibrational energy level is indicated by recent work.[2,3] Both semiempirical[12-14] and ab initio[4-7,15-19] treatments of carbon