to support the charge required to completely fill the 1e orbitals, the $2n + 2$ framework electron borane dianions $B_8H_8^{2-}$ and $B_9H_9^{2-}$ are well-known and readily prepared.[41,47]

For the chlorides, however, the situation differs because of the contributions of the tangential chlorine 3p atomic orbitals. The reduction of the neutral species, B_nCl_n, would result in the occupation of the 2e (B_4Cl_4), $8b_2$ (B_8Cl_8), and $3a_2'$ (B_9Cl_9) orbitals. These orbitals correspond to the orbitals of the hydride anions in symmetry, but in the highest occupied $B_8Cl_8^{2-}$ and $B_9Cl_9^{2-}$ orbitals there is also a significant contribution that is derived from the Cl ligand group orbitals; see Table V. In each case this component is antibonding with respect to the boron framework. In the boron halide dianions, the occupation of the HOMO orbitals increases the boron–boron bond strength, but it simultaneously weakens the B–Cl bonding; see Table IV.

Examination of the core overlap population of the $1a_2'$ (HOMO) orbital of $B_9H_9^{2-}$ obtained from the INDO calculations confirms that this orbital is strongly boron–boron bonding; the average core overlap population in this orbital is +0.081. The B–H overlap in the $1a_2'$ orbital is, of course, 0; see Table V. For $B_9Cl_9^{2-}$ (prism height 1.81 Å), however, the INDO results indicate that the average B–Cl bond overlap population in the $3a_2'$ (HOMO) orbital is negative, −0.010. The average core overlap population in this orbital is positive, but only 0.047.

Thus the Hoffmann–Lipscomb approach,[49] which involves separating intracage from ligand–cage interactions, and the framework electron counting schemes, which explicitly or implicitly utilize this type of factorization, are successful in the borane dianions $B_8H_8^{2-}$ and $B_9H_9^{2-}$ because the highest occupied molecular orbitals in these species are totally framework bonding. These frontier orbitals are in fact best described as the $(n + 1)$th framework bonding molecular orbitals; see Table V. Neutral B_8H_8 and B_9H_9, if formed, would be expected to be exceptionally electrophilic.

In the boron chlorides, however, the framework electron counting rules are less successful because the underlying approximation is less valid. This is due to the antibonding contributions of the tangential Cl 3p atomic orbitals. The genesis of the antibonding overlaps is that well over half of the available molecular orbitals are filled. The practical result of the differences in the bonding between the two types of cluster is that B_8Cl_8 and B_9Cl_9 are less electrophilic than the analogous hydrides. For the chlorides both the neutral and the 2− oxidation states are chemically accessible. For the hydrides only the 2− clusters, $B_8H_8^{2-}$ and $B_9H_9^{2-}$, have been isolated to date.

Acknowledgment. We thank Prof. Michael Zerner (University of Florida) for providing the enlarged INDO program required for the B_8Cl_8 and B_9Cl_9 calculations. Support of this work by the National Institutes of Health, the National Science Foundation, the donors of Petroleum Research Fund, administered by the American Chemical Society, The American Cancer Society and the Computer Center of the University of Illinois at Chicago is gratefully acknowledged.

Electron Density Analysis of the Reaction of Aldehydes with Lithium Hydride. The General Importance of the HOMO–HOMO Interaction

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Abstract: The transition states for the reactions of formaldehyde and acetaldehyde with lithium hydride were calculated at the restricted SCF level by using the 3-21G* basis set. Integrated electron population analysis indicates that lithium carries a charge of +0.85 in the transition state, nearly the same as in ground-state organolithium compounds. Molecular orbital analysis of these transition states reveals their HOMOs to be formed from both HOMO–LUMO and HOMO–HOMO interactions. The general importance of the HOMO–HOMO interaction is also shown through analysis of the transition state of the 1,3-cycloaddition of HCNO with acetylene.

Many theoretical studies of ground-state organolithium compounds have been reported in the recent literature. These studies indicate that the carbon–lithium bond is primarily ionic with only a small covalent component.[1] Coulomb's law alone reasonably predicts and explains the large number of experimentally and theoretically determined organolithium structures. We now turn to other states to see if ionicity remains dominant; in particular, does lithium act as a full cation in the transition state of a reaction involving organolithium compounds? Recent theoretical[2] and computational[3] advances have provided the opportunity to fairly readily calculate transition-state geometries. This report focuses on the electronic description of lithium compounds during the course of a reaction with emphasis on the transition state. In particular, we investigate the 1,2-addition of an organolithium reagent to a carbonyl by examining the prototypical reaction—lithium hydride addition to formaldehyde to form lithium methoxide (eq 1). Furthermore, molecular orbital analysis of the transition state points out a fundamental error inherent in many frontier molecular orbital applications.

$$H_2CO + LiH \rightarrow H_3COLi \qquad (1)$$

Computational Methods

The calculations reported in this work were carried out by using the GAUSSIAN-82[3] package on a VAX-11/750. All structures were optimized at the restricted SCF level by using the 3-21G* basis set.[4] The transition

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(1) For reviews, see: (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (b) Bachrach, S. M.; Streitwieser, A., Jr.; Schleyer, P. v. R., unpublished results.

(2) (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225. (b) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1982**, *77*, 5647. (c) Cerjan, C. J.; Miller, W. H. *J. Chem. Phys.* **1981**, *75*, 2800.

(3) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., unpublished results, Carnegee-Mellon University.

(4) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. Exponents for the polarization functions were $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.8$.

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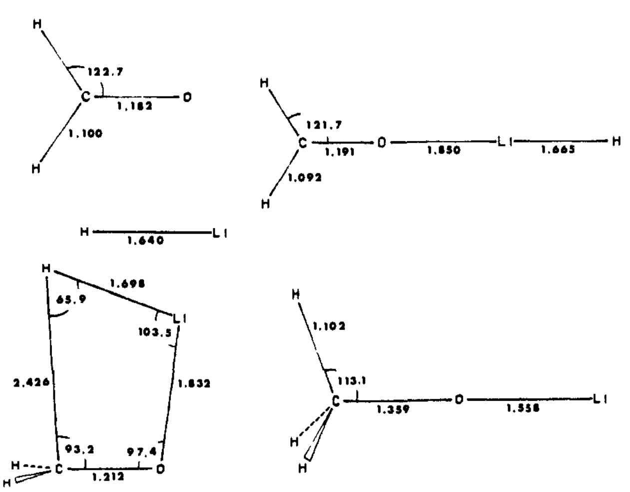

Figure 1. Geometry of the four critical points along the reaction of formaldehyde with lithium hydride: (a, top left) reactants, (b, top right) coordination state, (c, bottom left) transition state, (d, bottom right) product. All distances in angstroms and angles in degrees.

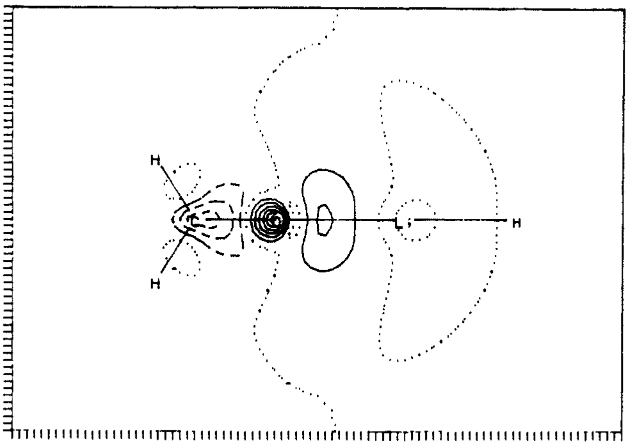

Figure 2. Projected electron density difference map formed by subtracting formaldehyde and LiH from the coordinated state. Contour levels from −0.03 to 0.05 by 0.01 e au^{-2}.

structures obtained here were confirmed by obtaining the analytical force constants, of which one was negative. Integrated spatial electron populations (ISEP) and density maps were obtained by using PROJ[5] and the integration[6] programs developed for the Tektronix 4050 series computers.

Geometries and Energetics

Kaufmann and Schleyer[7] have recently examined the reaction of lithium hydride with formaldehyde by using the 3-21G and 6-31G* basis sets, and we have substantiated their results with the 3-21G* basis set. Two critical structures are obtained along the pathway. Lithium hydride and formaldehyde combine in a linear fashion to form a stable complex. The optimized geometry of this "coordinated" state at 3-21G* is given in Figure 1. This complex is formed by alignment of the dipoles of each molecule to maximize the electrostatic attraction, with very little change in the geometry of the fragment molecules. Figure 2 presents the projected electron density difference formed by subtracting the projected electron densities of formaldehyde and lithium hydride from the density of the coordinated complex. The small levels of the difference contours indicate that the density distribution of formaldehyde and lithium hydride changes very little upon coordination. Furthermore, the two highest occupied MOs of the coordinated state are essentially identical with the HOMOs of the separated molecules. This "coordinated" state is a minimum on the surface but only locally.

Table I. Reaction Parameters[a]

parameter	coordination state	transition state	product	Δ[b]
r(C–O)	1.1909	1.2124	1.3590	0.128
(H–C–H)	116.6	115.7	105.6	0.081
a[b]	0.0	4.71	49.6	0.095

[a] All distances in angstroms and all angles in degrees. [b] See text for definition of these parameters.

Table II. Relative Energies (kcal mol^{-1}) of the Critical Points for the Reaction of LiH with Formaldehyde

	rel energy		
system	3-21G[a]	3-21G*[b]	6-31G*[a]
H_2CO + LiH	0.0	0.0	0.0
coordination state	−29.3	−25.19	−19.8
transition state	−22.1	−19.96	−16.2
H_3COLi	−71.5	−54.51	−55.0

[a] Reference 7. [b] This work.

Table III. Net Atomic Charge from ISEP for All Atoms at the Critical Points for the Reaction of LiH with Formaldehyde

	O	Li	H	C
H_2CO + LiH	−1.22	+0.86	−0.85	+1.22 (CH_2)
coordination state	−1.29	+0.85	−0.88	+1.33 (CH_2)
transition state	−1.23	+0.86	−0.79	+1.17 (CH_2)
H_3COLi	−1.34	+0.84	+0.51 (CH_3)	+0.51 (CH_3)

The next step along the pathway is the rotation of lithium hydride, bringing the hydrogen of lithium hydride toward the carbon atom. The structure of the transition state at 3-21G* is given in Figure 1. Analysis of the force constants showed one and only one force constant to be negative, with a frequency of 240i cm^{-1}, indicating that this structure is indeed a transition state. The transition structure has a very long carbon–hydrogen interaction (2.426 Å). The lithium–hydrogen bond has lengthened by only 0.06 Å at the transition state. Both of these distances indicate an "early" transition state. Additional information on the extent of reaction at the transition state is provided through analysis of the structural changes that occur during the reaction. In Table I we present the values of three structural parameters at the coordination state, the transition state, and product state. These parameters are the C–O bond length, the H–C–H angle, and a, the angle between the plane perpendicular to the molecular symmetry plane and the plane formed by the H–C–H angle. The last column (labeled Δ) is the difference between the coordination state and the transition state divided by the difference in the coordination state and the product. These three ratios are similar, indicating that the geometrical changes occur nearly synchronously. These small values confirm that the transition state is geometrically quite early, approximately 10% along the reaction pathway. The reaction then proceeds to lithium methoxide, primarily through the formation of the carbon–hydrogen bond.

The energy of this reaction is given in Table II. The formation of the coordinated state is exothermic by 25 kcal mol^{-1}, which originates primarily from the electrostatic attraction of the dipoles. The transition-state energy is reached through a loss of Li–H bonding and the nonlinear electrostatic alignment. The products lie 34 kcal mol^{-1} below the transition state, making the overall reaction 54.4 kcal mol^{-1} exothermic. The 3-21G* results are consistent with the 6-31G* calculations; however, the 3-21G results are significantly different. Schleyer[7] suggests that large superposition errors occur with the small 3-21G basis set, which artificially stabilize the coordinated state, the transition state, and the product. Note that this pathway does not have a transition state lying above the energy of the reactants.

Electron Population

The net charges for each atom at the four critical points (reactants, coordinated state, transition state, products) are

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(5) Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D. L.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2499.

(6) McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comp. Chem.* **1985**, *9*, 165–169.

(7) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560.

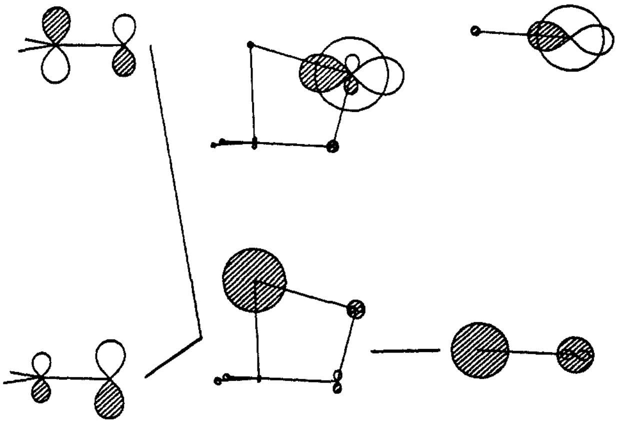

Figure 3. Atomic orbital diagram of the frontier orbitals of formaldehyde, the transition state, and lithium hydride.

presented in Table III. Net charges are obtained through the ISEP[5] procedure using a line of demarkation that follows the minimum electron density path[6] between atoms. This procedure is not capable of reasonably separating the electron density between carbon and hydrogen for normal C–H bonds because of the short C–H distance.[8]

As with other lithium compounds,[9] lithium carries an approximate charge of +0.85 throughout the course of the reaction, remaining at all times essentially a positive counterion. Oxygen carries a −1.22 charge in formaldehyde but becomes more negative as the reaction goes toward lithium methoxide. Clearly, the product lithium methoxide is an ion pair, and since oxygen is the most electronegative atom in the system, it carries most of the anionic charge of methoxide. It is reasonable, therefore, that oxygen gains electron density during the reaction. The hydrogen from lithium hydride loses electron density during the reaction as it goes from a hydride anion to a carbon-bound atom. In general, the distribution of charge is as expected, confirming that lithium is essentially a cation at all times.

Although correlation effects are not considered in these calculations, we do not anticipate the addition of correlation effects to change significantly the electron density distribution in the transition state. The transition state is essentially comprised of two closed shell ions interacting via simple electrostatics and does not, therefore, require the inclusion of correlation for accurate description. Certainly correlation will affect the energetics, perhaps to even lower the transition state below the coordination state, but the density analysis performed here at the SCF level should be a good approximation of the actual correlated density.

The electron populations offer an alternative method for determining the extent of reaction. The change in hydride population is 0.09 e in proceeding from the coordination state to the transition state. Unfortunately, we cannot obtain the H population in the product due to the inability to effectively separate the C and H densities. If, however, the electron transfer mirrors the geometrical changes, the hydrogen charge should be essentially neutral. More probably, the hydrogen is actually somewhat negative, tentatively suggesting that the amount of charge transfer exceeds the degree of structural changes in proceeding to the transition state. Further studies using this type of analysis are currently under way.

Molecular Orbital Analysis

Frontier molecular orbital (FMO) theory[10] has been quite successful in explaining the mechanisms of a wide variety of organic reactions. The reaction of formaldehyde and lithium hydride involves small and well-understood molecules. FMO theory should be able to explain the transition state of the reaction, especially since the transition state is early.

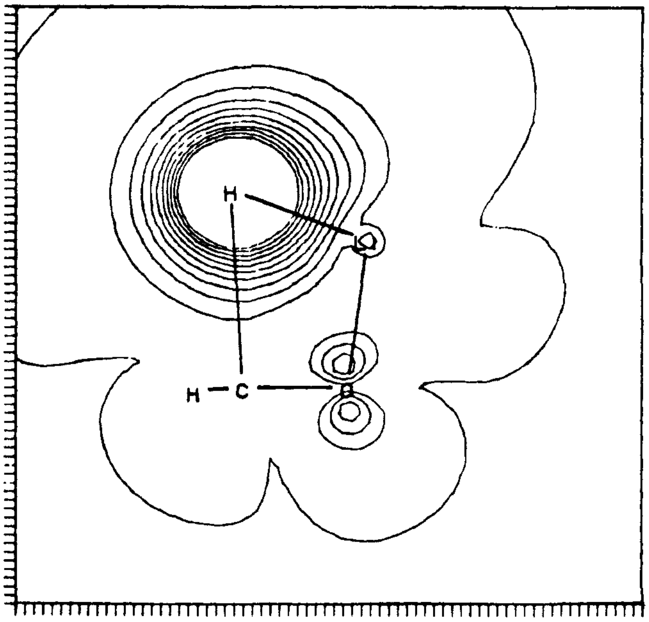

Figure 4. Projected electron density of the HOMO of the transition state of the reaction of formaldehyde with lithium hydride. Contour levels from 0.0001 to 0.1001 by 0.01 e au^{-2}.

The transition state should be analyzed by using the MOs of the coordinated state, since the coordinated state is really the "reactant". However, as shown previously, the highest occupied MOs of the coordinated state are virtually identical with the HOMOs of formaldehyde and lithium hydride. It is also conceptually easier to refer to reactant MOs rather than to the MOs of the coordinated state. Thus, we shall use the reactant MOs for the FMO analysis.

The frontier orbitals of formaldehyde and lithium hydride are shown in Figure 3. FMO theory predicts the predominant interaction will be the HOMO of lithium hydride with the LUMO of formaldehyde. Thus, the HOMO of the transition state is expected to have large electron density on hydrogen, substantial p-type density on carbon with a smaller p-type density on oxygen, and little density on lithium. This, however, is not what is found. The projected electron density of the HOMO of the transition state is presented in Figure 4, and its atomic orbital description is given in the center of Figure 3. The transition-state HOMO is comprised of little carbon electron density and significant oxygen p-type and hydrogen electron densities. The transition-state HOMO is not formed from just a simple HOMO–LUMO interaction, but rather the HOMO of lithium hydride interacts with a linear combination of the HOMO and LUMO of formaldehyde. This linear combination (formed by the addition of the HOMO and the LUMO) essentially cancels the carbon coefficient and enhances the oxygen coefficient. The transition state is not solely dominated by a HOMO–LUMO interaction; the HOMO–HOMO interaction also plays a major role. This HOMO–HOMO interaction ensures that electron density is transferred from the hydride to the oxygen.

In order to confirm this large HOMO–HOMO interaction, we applied perturbational molecular orbital (PMO) theory.[11] FMO theory relies on the fact that the extent of orbital interaction is inversely proportional to the separation of their energies. If we want the HOMO of formaldehyde to interact more strongly with the HOMO of lithium hydride, we somehow have to raise the energy of the formaldehyde HOMO. PMO theory suggests that electron donor groups will raise the energy of the HOMO. The

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(8) For further discussion of integrated population analysis, see: Bachrach, S. M.; Streitwieser, A., Jr., unpublished results.

(9) (a) Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. In *Electron Distribution and the Chemical Bond*; Coppens, P., Hall, M. B., Eds.; Plenum: New York, 1982. (b) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818.

(10) (a) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (b) Houk, K. N. *Acc. Chem. Res.* **1975**, *11*, 361.

(11) (a) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969. (b) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

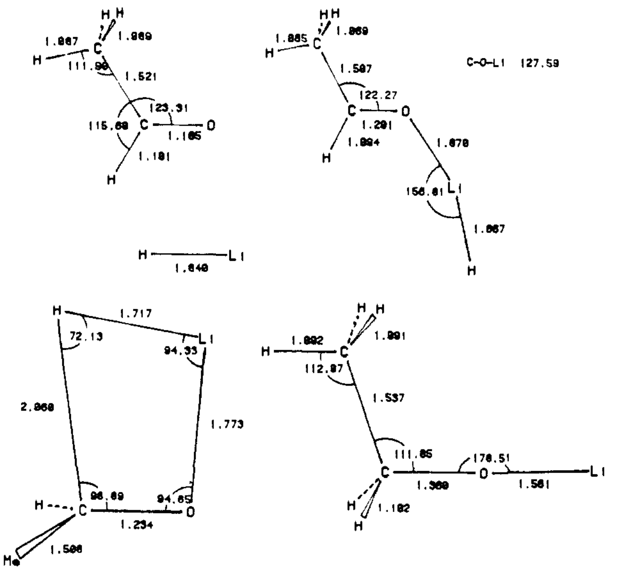

Figure 5. Geometry of the four critical points along the reaction of acetaldehyde with lithium hydride: (a, top left) reactants, (b, top right) coordination state, (c, bottom left) transition state, (d, bottom right) product. All distances in angstroms and all angles in degrees.

Table IV. Relative Energies (kcal mol^{-1}) of the Critical Points for the Reaction of LiH with Acetaldehyde

system	rel energy	system	rel energy
$CH_3CHO + LiH$	0.0	transition state	−20.57
coordination state	−29.00	CH_3CH_2OLi	−51.05

simplest electron-donating group to add to formaldehyde without significantly perturbing its chemistry is a methyl group. Therefore, we determined the structure and energy of the four critical points along the pathway of the reaction of acetaldehyde with lithium hydride (eq 2). The HOMO of this transition state should involve

$$CH_3CHO + LiH \rightarrow CH_3CH_2OLi \qquad (2)$$

significant participation of the HOMO of acetaldehyde. In particular, we expect more electron density on oxygen in the acetaldehyde case than in the formaldehyde case.

The geometry of the critical points for the reaction of acetaldehyde with lithium hydride at 3-21G* is presented in Figure 5. The shorter C–H and O–Li distance of this transition state suggests that it is somewhat further along the path than the transition state of formaldehyde with lithium hydride. Further, the ratios Δ for the C–O distance and the Me–C–H angle are 0.207 and 0.208, respectively. These ratios, although still small, are larger for the acetaldehyde case than for formaldehyde, suggesting that the acetaldehyde transition state is still early but further along the reaction pathway than the formaldehyde transition state. Additionally, charge transfer from hydride is larger for the acetaldehyde transition state (0.12 e) than for the formaldehyde transition state (0.09 e).

The energetics of the acetaldehyde reaction are given in Table IV. As with the formaldehyde case, acetaldehyde and lithium hydride first complex to a coordinated state formed by alignment of their dipoles, releasing some 29 kcal mol^{-1}. Lithium hydride then rotates to the transition state, gaining about 8.5 kcal mol^{-1} in the process. The reaction then proceeds to product with an overall exothermicity of 51 kcal mol^{-1}. Again, this reaction does not have a transition state energetically higher than the reactants.

The frontier molecular orbitals of acetaldehyde and lithium hydride are shown in Figure 6. Again, using FMO theory, we expect the HOMO of the transition state to be formed from the interaction of the HOMO of lithium hydride with the LUMO of acetaldehyde. FMO theory predicts the transition-state HOMO to have large electron density at hydrogen and predicts carbon and oxygen p-type densities of nearly similar size. Figure 7 shows the projected electron density of the transition-state HOMO, along with its atomic orbital description in the center of Figure 6. The HOMO of lithium hydride interacts with a linear combination formed by subtracting the HOMO from the LUMO of acetaldehyde. This linear combination will essentially cancel the carbon coefficient and produce a large oxygen coefficient. The large electron density on oxygen indicates a major role for the acetaldehyde HOMO. In fact, there is significantly more density on oxygen in the acetaldehyde transition-state HOMO than in the formaldehyde case, confirming the PMO prediction that electron donor groups would increase the HOMO–HOMO interaction.

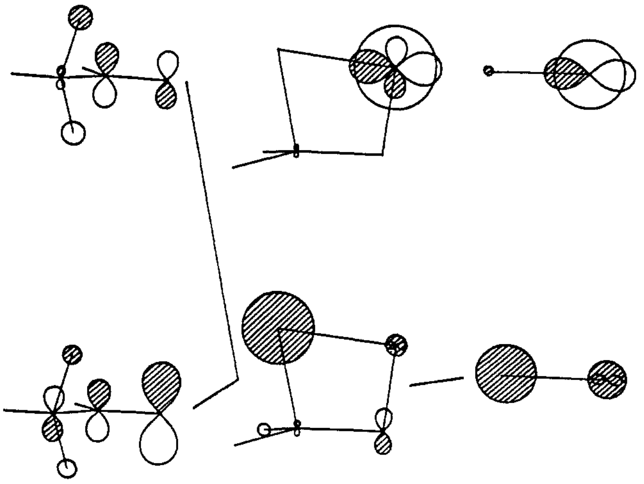

Figure 6. Atomic orbital diagram of the frontier orbitals of acetaldehyde, the transition state, and lithium hydride.

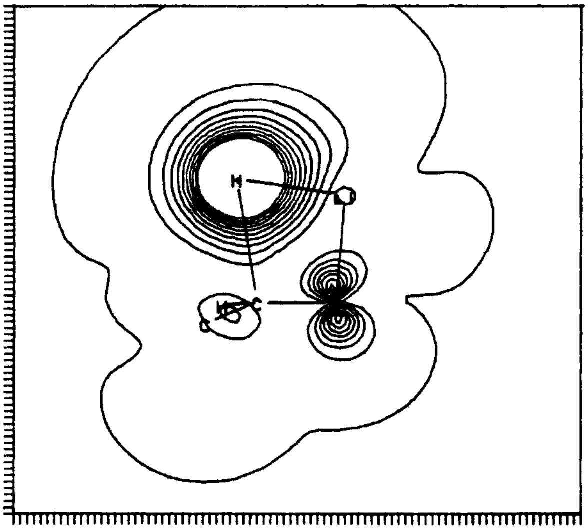

Figure 7. Projected electron density of the HOMO of the transition state of the reaction of acetaldehyde with lithium hydride. Contour levels from 0.0001 to 0.1001 by 0.01 e au^{-2}.

Hoffmann[12] and Fukui[13] have discussed the possibility of the participation of the HOMO–HOMO interaction in terms of perturbation theory. Their argument starts by assuming two noninteracting species, A (donor) and B (acceptor). When these systems interact to form a transition state, the first-order interaction will involve intermolecular orbital mixing. The standard HOMO–LUMO interaction is, thus, a first-order orbital mixing process and involves, for example, the HOMO of A and the LUMO of B. Second-order orbital mixing occurs via intramolecular mixing; for example, the HOMO and LUMO of B will interact in second-order as will the HOMO and LUMO of A. The HOMO–HOMO interaction is a second-order interaction in this

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[12] Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

[13] Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

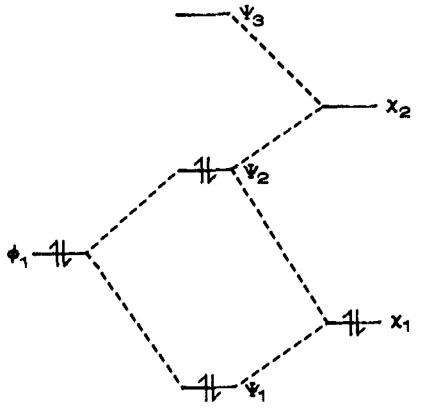


Figure 8. Modified frontier molecular orbital interaction diagram.

approach; that is, the HOMO of A interacts with the LUMO of B (first order) which then interacts with the HOMO of B (second order). This is a three-orbital process but occurs in second order.

It is important to note that the above argument pertains to the *net energies* of the systems. Individual wave functions, however, are subject to much greater changes on perturbation. For example, the HOMO of A will combine in the usual plus and minus manner with the HOMO of B, given allowed symmetry, and the minus combination will be the new HOMO. Since this is a filled–filled orbital interaction, the net energy change is small, but the change in the wave functions is first order. In fact, since the two HOMOs will generally be closer in energy than a HOMO and LUMO, the effect of the HOMO of B on the HOMO of A will generally be *greater* than the effect of the LUMO of B; however, the filled–unfilled nature of the HOMO–LUMO interaction will generally have a greater energy consequence. It is the contribution of the HOMO of B to the new HOMO of the perturbed A that provides the second-order energy interaction with the LUMO. Indeed, any property that is summed over all of the occupied MOs will include both the plus and minus filled–filled orbital combinations and will show only a second-order effect. Nevertheless, the FMO approach to any further perturbation, such as the effect of substituents, must take cognizance of the new HOMO.

Examination of the orbital density plots clearly shows the extent of the HOMO–HOMO interaction to be as large as the HOMO–LUMO interaction. The HOMO–HOMO wave-function interaction is not a second-order interaction. Simple FMO applies only to net energetics and does not properly predict the extent of orbital mixing. Of course, perturbation theory holds only for cases where the perturbation (i.e., the interaction) is small. Formation of a transition state is not necessarily a small perturbation. Dramatic changes in bonding and electronic distribution can occur during a reaction. FMO theory may fail even with respect to net energy when the interaction of two systems at the transition state is too large for perturbation theory to apply.

Recently, Bach and Wolber[14] have shown the important role of HOMO–HOMO interactions in nucleophilic substitution at vinylic carbons, the trimerization of acetylene, and S_N2 and S_N2' displacements. They considered the transition state of a reaction to be determined by an interplay of two-electron (HOMO–LUMO) and four-electron (HOMO–HOMO) interactions. FMO theory usually ignores the four-electron interaction, since it is overall destabilizing, and concentrates on the two-electron HOMO–LUMO stabilizing interaction. Bach and Wolber point out that the four-electron splitting is frequently much larger than the two-electron splitting since the orbitals involved in the four-electron case (the two HOMOs) are usually much closer in energy then in the two-electron case (HOMO–LUMO). Consequently, when the HOMOs are of similar energy, the four-electron interaction will have a significant effect on the overall energetics.

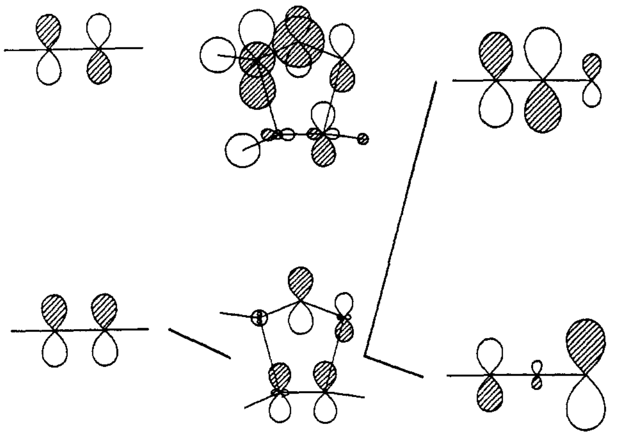


Figure 9. Atomic orbital diagram of the frontier orbitals of acetylene, the transition state, and fulminic acid.

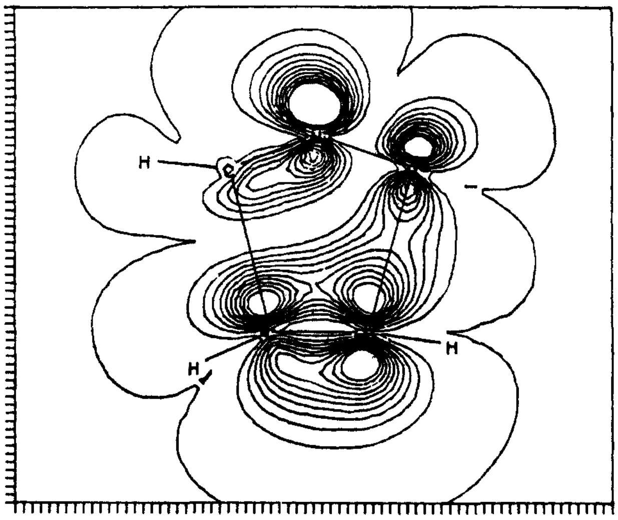
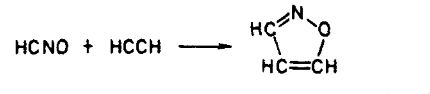


Figure 10. Projected electron density of the HOMO of the transition state of the reaction of acetylene with fulminic acid. Contour levels from 0.0001 to 0.1001 by 0.01 e au^{-2}.

Bach and Wolber offer the frontier orbital interaction diagram in Figure 8 as an alternative view for the formation of the transition state. A four-electron interaction between the two HOMOs, ϕ_1 and χ_1, occurs. This results in the dramatically stabilized MO ψ_1 and the destabilized "effective HOMO" ψ_2. This higher MO ψ_2 can now interact more strongly with the LUMO χ_2 to produce a more energetically stabilizing two-electron interaction. The approach is effectively the same as the perturbation discussion above but emphasizes that the four-electron HOMO–HOMO energy interaction can have important magnitude even if it is of second order.

We may next inquire as to the general applicability of HOMO–HOMO interactions compared to HOMO–LUMO. Frontier molecular orbital theory has generally had excellent success in explaining the mechanism of cycloaddition reactions and, more specifically, the regio- and stereochemistry of these reactions. Komornicki et al.[15] have determined, at the 4-31G and DZ SCF levels, the transition-state geometry for the reaction of acetylene with fulminic acid to give isoxazole (eq 3).



(3)

We have calculated the projected electron density for this structure at the 4-31G level. Figure 9 presents the frontier orbitals

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[14] (a) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1401, 1410. (b) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1985**, *107*, 1352. (c) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837.

[15] Komornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

J. Am. Chem. Soc. **1986**, *108*, 3951-3960

of acetylene and fulminic acid. FMO analysis predicts the transition-state HOMO to be formed from the interaction of the acetylene HOMO with the LUMO of fulminic acid, suggesting little p-type density on oxygen and large p-type density on the carbon and nitrogen of the fulminic acid fragment. The projected electron density of the transition-state HOMO is given in Figure 10. The HOMO shows large oxygen and nitrogen p-type densities and very little density on carbon. The acetylene HOMO actually interacts with a linear combination formed by the addition of the fulminic acid HOMO and LUMO. This prototypical 1,3-cycloaddition certainly involves significant HOMO–HOMO interaction.

Additionally, the involvement of the HOMO–HOMO interaction explains a peculiarity noted by Komornicki et al. They performed a force constant analysis of the transition state and noted the force constant along the forming C–O bond to be about 10 times as large as the force constant along the forming C–C bond.[16] The electron density map of the transition-state HOMO (Figure 10) clearly indicates considerable density in the region forming a bond between carbon and oxygen but little density in the region forming the C–C bond. FMO theory predicts a stronger C–C interaction than C–O on the basis of the coefficients in the fulminic acid LUMO. This is obviously invalid and is corrected by adding in the HOMO of fulminic acid to create a sizable oxygen coefficient while significantly reducing the carbon coefficient.

Conclusion

Evidently, the FMO approximation of HOMO–LUMO interactions dominating the transition state is too severe. The HOMO–HOMO interaction must be included to obtain adequate description. The HOMO of the transition state is determined primarily from the HOMO–HOMO interaction of the reactants. The *energy* of the transition state is determined by LUMO interactions as well.

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Registry No. H_2CO, 50-00-0; LiH, 7580-67-8; CH_3CHO, 75-07-0; HCCH, 74-86-2; HCNO, 506-85-4.

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(16) Some controversy exists concerning the definition of the force constants in the transition state of this reaction; see: Hiberty, P. C.; Ohanessian, G.; Schlegel, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 719.

Hyperstable Olefins: Further Calculational Explorations and Predictions

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Abstract: Although olefins at bridgehead positions are generally destabilized by strain, such locations may actually be preferred in larger polycyclic systems. A large number of such hyperstable bridgehead olefins have been explored by using Allinger's MM2 force field to calculate heats of formation and strain energies. In addition to monoolefins, systems with two double bonds at bridgeheads and tetracyclic olefins are predicted to be hyperstable. "In" rather than "out" pyramidalization of saturated bridgehead carbons in both bridgehead olefins and in the parent hydrocarbons is favored in several instances. The most stable bridgehead olefin (*E* isomer of out bicyclo[4.4.3]trideca-1-ene) and double bridgehead diene (*EE* isomer of bicyclo[4.4.3]trideca-1,6-diene) studied have olefin strains of −16.8 and −31.7 kcal/mol, respectively. Two tetracyclic olefins (tetracyclo[$8.4.4.4^{3,8}.0^{2,9}$]docosan-2(9)-ene, and tetracyclo[$9.5.5.5^{3,9}.3^{2,10}$]hexacosan-2(10)-ene) are predicted to have *endothermic* cis heats of hydrogenation.

Bridgehead olefins have fascinated chemists ever since Bredt noted that double bonds avoid the ring junctions in camphane and pinane systems.[1,2] Recently, Maier and Schleyer recognized that the reverse can be expected in medium-size polycyclic ring systems where bridgehead double bonds may actually be preferred.[3] These "hyperstable olefins" have *negative* olefin strain energies (OS): the strain energy of the olefin is *less* than that of its parent hydrocarbon. A qualitative correlation was found between calculated (MM1 force field) OS values, which measure the thermodynamic driving force toward reaction, and experimentally observed stabilities and reactivities.[3a] Due to their negative OS values, hyperstable bridgehead olefins have heats of hydrogenation ΔH_{hyd} lower than normal (i.e., the values found for acyclic olefins with the same degree of substitution); these ΔH_{hyd} are even lower than those of medium size ring cycloalkenes (Table I).[5,6]

Several hyperstable bridgehead olefins were reported shortly after Maier and Schleyer's paper appeared. The predicted hyperstability of bridgehead olefins in medium size ring systems[3a] was first experimentally corroborated by de Meijere et al.'s ob-

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(1) Bredt, J.; Thoret, H.; Schmitz, J. *Liebigs Ann. Chem.* **1924**, *437*, 1.

(2) Reviews: (a) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic: New York, 1978. (b) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. III, Chapter 5, p 299. Also see ref 9.

(3) (a) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891. (b) Warner, P. M.; Peacock, S. *J. Comput. Chem.* **1982**, *3*, 417. (c) Precedents are found in the enhanced stability of planar bridgehead centers in medium size polycyclic ring systems in carbocations: Parker, W.; Trouter, W. C.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121. The flattened bridgehead position of bicyclo[3.3.3]undecane (Manxane) system: Murray-Rust, P; Murray-Rust, J.; Watt, C. I. F. *Tetrahedron* **1980**, *36*, 2799. Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136. Coll, J. C.; Crist, D. R.; Barrio, M. d. C. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 7092. And flattened amine groups at bridgehead positions (ref 4). Also see: Bly, R. S.; Hossain, H. M.; Leboida, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549.