

Electronic aspects of the hydride transfer mechanism. *Ab initio* analytical gradient studies of the cyclopropenyl-cation/lithium hydride model reactant system

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The electronic mechanisms of a model hydride transfer reaction are theoretically studied with *ab initio* RHF and UHF SCF MO procedures at the 4-31G basis set level and analytical gradient methods. The model system describes the reduction of cyclopropenyl cation to cyclopropene by the oxidation of lithium hydride to lithium cation. The molecular fragments corresponding to the asymptotic reactive channels characterizing the stepwise mechanisms currently discussed in the literature have been characterized. The binding energy between the fragments is estimated within a simple electrostatic approximate scheme. The results show that a hydride-ion mechanism is a likely pathway for this particular system. The system is thereafter thoroughly studied from the supermolecule approach. Reaction paths for the ground and first triplet electronic states have been calculated. The hypersurface is explored from a geometrical disposition of the reactants that mimics the one found in several dehydrogenases (perpendicular configuration). A hydride ion is found to be the particle transferred on the unconstrained as well as the constrained reaction pathways in the ground electronic state. In the triplet state (perpendicular configuration) the mechanism is stepwise: electron transfer followed by a hydrogen atom transfer. It has been noticed that the perpendicular geometrical disposition of the reactants plays an important role by polarizing the susceptible cyclopropene C-H bond in the sense of increasing the electronic density at the hydrogen nucleus. This provides a clue to rationalize several dehydrogenase's active site structure and mechanism. The reactant molecular complex found in the inverted potential energy curves, namely the $\text{LiH}\cdots\text{Cp}^+$ association has an electronic distribution which can be described as a hydride ion cementing two electron deficient centers corresponding to the cyclopropenyl and the lithium cations. Direct CI calculations confirm the overall picture obtained above.

I. INTRODUCTION

Hydride transfer processes play significant roles in biological redox systems. This type of reaction has been thoroughly characterized structurally in alcohol dehydrogenase¹ and frequently discussed in electronic terms.² There the reaction is the oxidation of an alcoholic group by nicotinamide adeninedinucleotide (NAD^+). Although, at the molecular level the stereochemical course of the reaction is fairly well known,¹ the electronic nature of the hydride transfer step remains controversial.²⁻⁶ Currently, three mechanisms have been proposed and discussed relative to the experimental kinetic information³⁻⁵: (a) electron-proton-electron pathway ($e^- - \text{H}^+ - e^-$); (b) electron-hydrogen atom transfer (or its reverse); and (c) the one-step hydride ion transfer all along the reaction path. Since the issue is hard to settle experimentally,⁶ theoretical work can help solving this important problem. Unfortunately, a quantum mechanical characterization of the reaction pathways in the supermolecular approach for each of the available channels is a very difficult task. This is even more difficult if one wants to study realistic molecular models. In this paper the reactive hypersurface of a carefully chosen model system in its ground electronic state is studied. The model includes some aspects relevant to dehydrogen-

ases reactions and it is simple enough to allow for extensive *ab initio* analytical gradient calculations. The study of the reactive hypersurface may help understanding the electronic properties of the hydride acceptor center of typical dehydrogenase reactions. Furthermore, in order to get a complete description of the contending mechanisms a simplified diabatic procedure is proposed. This one involves the *ab initio* analytical gradient calculation of the molecular fragments that characterize the asymptotic reactive channels for a given electronic mechanism. The work necessary to assemble the molecular partners at a given distance and orientation is assumed to be dominated by the electrostatic interactions between the charged species. The procedure is tested against the adiabatic results and extended to more realistic situations.

A number of quantum chemical calculations on hydride ion-molecule reactions have already been reported.⁷⁻¹¹ In particular, reactions of hydride-ion exchange with methane and fluoromethane have been calculated with large basis sets including polarization functions.¹¹ However, most of these systems are not very relevant to biochemical situations. Quantum chemical studies of biologically significant model systems¹² have been reported at a minimal basis set level only. Unfortunately, the use of minimal basis sets in a study designed to accept or reject an electronic mechanism concerning global hydride transfer reactions is questionable. As it will be shown later on, a physically plausible representa-

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tion of a hydride ion requires at least medium size basis set (double zeta type). Due to computing expenses larger basis set are not adequate if one wants to extend the procedures to study realistic model systems.

The adiabatic and diabatic-like approaches are applied to study the model reaction between lithium hydride (LiH) and cyclopropenyl cation (CP⁺). A particular attention is given to the way the internal geometry of the ring system and the intermolecular orientation determine the hydride pathway. The 4-31G basis set has been chosen as the lowest level for representing the wave function. To what extent this basis set at the Hartree-Fock level affords a physically acceptable description of hydride exchange reaction is one of the issues addressed. The limitation of the basis set size is imposed by the huge amounts of central processor unit time of a Cyber 170/835-type required to carry out the geometrical optimizations.

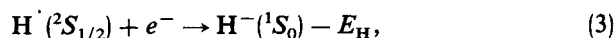
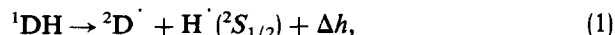
In the following section the diabatic scheme is described briefly. The model and method are introduced in Sec. III. In Sec. IV the results obtained with the diabatic scheme and adiabatic supermolecule framework are presented and discussed. The spin triplet hypersurface is partially explored to get an insight of the electronic nature of the hydride transfer in an excited electronic state. In Sec. V constrained minimum energy profiles for the perpendicular attack of LiH on CP⁺ are examined. This arrangement mimics the spatial disposition of the substrate and coenzyme in actual enzymatic systems.¹ Correlation effects and basis set reliability are discussed in Sec. VI, where results obtained by direct CI calculations for selected points of the energy hypersurface are presented and discussed. A general discussion closes the paper (Sec. VII).

II. ELECTRONIC MECHANISMS: THE DIABATIC SCHEME

For an overall hydride transfer reaction there are four pathways that lead to the same result, although they might have different energy requirements. They are: (A) Hydride-ion transfer from the donor DH to the acceptor A. (B) Hydrogen atom transfer followed by electron transfer: $\dot{\text{H}}-e^-$. (C) Transfer of an electron followed by a hydrogen atom: $e^- - \text{H} \cdot$. (D) Electron-proton-electron transfer: $e^- - \text{H}^+ - e^-$.

For any one of these pathways there is a bond breaking and bond forming process. Explicit electron transfer processes are present in all but the A mechanism. The mechanisms B and C have associated a homolytic bond breaking process. These two types of processes produce radical intermediates. In the spin singlet ground state, the electron transfer and homolytic bond breaking are related to the formation of spin doublet states. These doublets combine along the reaction path to produce singlet states. The energy necessary to produce the appropriate molecular species corresponding to these channels can be, in many cases, experimentally estimated. This is illustrated, for instance, by the following calculation required to obtain the information for the A mechanism. Here the DH bond dissociates into two ions (if DH is electrically neutral), each one of them having an electronic closed shell structure, e.g., H^- and A^+ . The energy for this

asymptotic channel can be calculated from the set of equations:



where h is the D-H bond dissociation energy; I_{D} is the ionization potential of the molecular fragment D; and E_{H} is the hydrogen atom electron affinity. In this work the geometry and the total electronic energy of the intermediates species, which are not usually experimentally known, are determined with *ab initio* analytic gradient methods.

The above calculation shows that the energy required to dissociate D-H into ions at infinite distance is $I - E$ above the homolytic rupture (B channel). Similar analysis can be made for the remaining channels, thereby leading to a numerical estimate of the energy gaps among them.

Since in real systems the transfer occurs at a particular intermolecular distance and orientation of the reactant partners DH and A the energy necessary to assemble the species in a putative transition state (TS) must be estimated.

It is generally accepted that a reasonable estimate of the complexation energy in ion-molecule interactions can be obtained from simple electrostatic calculations.¹³ For a neutral molecule having a permanent dipole moment and polarizability interacting with an ion of charge Q , the complexation energy is the sum of the charge-induced-dipole and charge-dipole interaction terms.¹³

For enzyme reactions both the intermolecular distance (R) and orientation are usually determined by the active site topography. The model system has been oriented according to the experimental information available. The electrostatic contribution to the interaction energy is given by

$$\Delta E = \sum_{\substack{j \in \text{A} \\ j \in \text{B}}} [Q_i Q_j / r_{ij} - \frac{1}{2}(Q_i \alpha_j + \alpha_i Q_j) / r_{ij}^4], \quad (4)$$

where $\{Q_i\}$ are the atomic effective charges obtained from the Mulliken population analysis, and $\{\alpha_i\}$ are atomic polarizabilities.¹³ The complexation energy can be estimated at a typical intermolecular distance R ; the position of the hydride-ion or the hydrogen atom in the putative transition states on the bridge is chosen (arbitrarily) as $R/2$.

Similar procedures must be used to estimate the energetics for the other pathways. We notice that the different mechanistic channels involve strong electrostatic interactions at one stage or another. One can expect that the differences in electrostatic energy will be the dominant factor that determines their relative energy. This is a strong approximation that has to be legitimated by comparisons with supermolecule calculations whenever these can be carried out.

III. MOLECULAR MODELS AND COMPUTING METHODS

A. Model system

The model system can be thought of as a pair of redox semireactions, namely LiH/Li^+ and $\text{CP}^+/\text{cyclopropene}$ (CPH), wherein two electrons and one proton are exchanged. The latter is assumed to mimic some aspects of the redox semireaction NAD^+/NADH , which involves, among other

things, electronic and geometrical reorganization at the C4 center and the bond system of the pyridinium ring.¹ Particular attention is given to the dependence of the ring geometry with the reaction coordinate pathway. By completing the redox system with the couple LiH/Li⁺ we have chosen to simplify as much as possible the electronic-geometric events taking place here.

The initial configuration has been chosen with the lithium atom sitting on top of C₁ in the plane perpendicular to the CP⁺ molecular plane with C_s symmetry. The energy hypersurface will always be explored from this initial configuration and the C_s symmetry is enforced during the geometrical optimizations.

B. Basis set and computational methods

The diffuse aspect of the hydride charge density^{14,15} is partially incorporated in the hydrogen basis set via the second component of the 1s orbital; this (1s'') component has a relatively small exponent (0.16). The diffuse aspect of the charge density can be sensed by the gross orbital charges on the 1s' and 1s'' which are for the hydrogen atom 0.37, 0.63, and for the hydride ion 0.37, 1.63, respectively. The energetic, however, is mediocre. The experimental electron affinity for hydrogen^{15c} is 0.75 eV while the 4-31G outcome is approximately -2.1 eV (cf. Table I).

For LiH(¹Σ⁺), multiconfigurational SCF MO calculations¹⁶ show that it dissociates as a pair of atoms in their spin

doublet states Li(²S_{1/2}) and H(²S_{1/2}). At equilibrium distance, however, the effective charge at the hydrogen nucleus is -0.57, and it remains negative (-0.42) after stretching the LiH 0.8 Å away from equilibrium.¹⁷ Comparisons with the results obtained with 4-31G or 6-31G basis sets, the latter is used as a check, show similar behavior as far as effective charges are concerned but quantitatively it underestimates them by approximately 50%.¹⁸ Therefore, the 4-31G basis set qualitatively discloses the presence of the anion-like center (via the excess charge density) although it underestimates the actual density.

Electronic open shell systems, spin doublets and triplets appearing along the asymptotic channels have been calculated in the unrestricted Hartree-Fock scheme, whereas a restricted HF method has been used for closed shell systems. As a general rule in this study, the geometry optimizations have been carried out until the average gradient length is below 10⁻⁴. Davidson's procedure is used for getting at minima,¹⁹ while maxima have been handled with the VA05AD procedure.²⁰ The calculations were carried out with the MONSTERGAUSS program²¹ on a CYBER 170/835 computer system at Uppsala Data Center.

IV. LIH/CYCLOPROPENYL SYSTEM: RESULTS

A. Diabatic scheme

The energy scheme for the associated asymptotic processes is summarized in Fig. 1. The optimized geometries,

TABLE I. (A) Geometry, total energy, average gradient lengths, and symmetry state of all fragments entering the various possible stepwise mechanisms for an overall hydride transfer for the model reaction CP⁺/CPH//LiH/Li⁺. Restricted HF framework for the singlets and unrestricted HF for the doublets and triplets have been used at a 4-31G basis set level. (B) Average value of S², effective charge, and spin density for all fragments reported in (A).

(A)		I: CP ⁺	II: CP ⁺	III: CP	IV: CPH	V: CPH	VI: CPH ⁺		
System		¹ A ₁	³ A ₂	² A ₁	¹ A ₁	³ B ₂	² B ₁		
Electronic state									
Distances (Å)	C ₁ -C ₂	1.3608	1.6458	1.4612	1.5121	1.4824	1.4683		
	C ₂ -C ₃	1.3608	1.2402	1.3060	1.2817	1.4957	1.3657		
	C ₁ -H	1.0636	1.0700	1.0554	1.0595	1.0792	1.0849		
	C ₂ -H	1.0636	1.0659	1.0602	1.0761	1.0594	1.0656		
Angles (deg)	<(C ₂ C ₁ C ₃)	60.00	44.27	59.09	50.15	60.58	55.46		
	<(HC ₁ H)	113.51	112.53	111.72		
	<(HC ₂ C ₁)	150.00	126.28	151.79	145.32	149.50	149.80		
Total energy (a.u.)		-114.816 447	-114.660 951	-114.993 893	-115.642 587	-115.561 321	-115.336 697		
Gradient length (average)		4.8 × 10 ⁻⁵	2.4 × 10 ⁻⁴	1.5 × 10 ⁻⁴	2.9 × 10 ⁻⁴	1.7 × 10 ⁻⁴	2.5 × 10 ⁻⁴		
System		VII: LiH	VIII: LiH ⁺	IX: Li [•]	X: Li ⁺	XI: H [•]	XII: H ⁻		
Electronic state		¹ Σ ⁺	² Σ ⁺	² S _{1/2}	¹ S ₀	² S _{1/2}	¹ S ₀		
Distances (Å)	Li-H	1.6370	2.4362		
Total energy (a.u.)		-7.977 349	-7.744 122	-7.428 465	-7.233 262	-0.498 233	-0.422 442		
Gradient length (average)		3.5 × 10 ⁻⁴	6.7 × 10 ⁻⁵		
(B)		I	II	III	IV	V	VI	VII	VIII
System									
<S ² >		0.0000	2.0324	0.7674	0.0000	2.0321	0.7586	0.0000	0.7500
C ₁	Q	-0.0336	-0.1765	-0.2806	-0.3231	-0.3617	-0.3914
	ρ ^s	0.0000	+1.9883	+1.1683	0.0000	-0.4060	-0.2449
C ₂	Q	-0.0336	-0.0120	-0.1883	-0.2026	-0.2215	+0.0062
	ρ ^s	0.0000	+0.0611	-0.0230	0.0000	+1.2102	+0.5341
H ₁	Q	+0.3669	+0.3688	+0.2178	+0.1525	+0.1931	+0.3294
	ρ ^s	0.0000	-0.1722	-0.1034	0.0000	+0.0948	+0.1192
H ₂	Q	+0.3669	+0.4158	+0.2197	+0.2118	+0.2093	+0.3601
	ρ ^s	0.0000	+0.0311	-0.0095	0.0000	-0.1020	-0.0308
Li	Q	+0.2642	+0.9472
	ρ ^s	0.0000	+0.0528
H	Q	-0.2642	+0.0528
	ρ ^s	0.0000	+0.9472

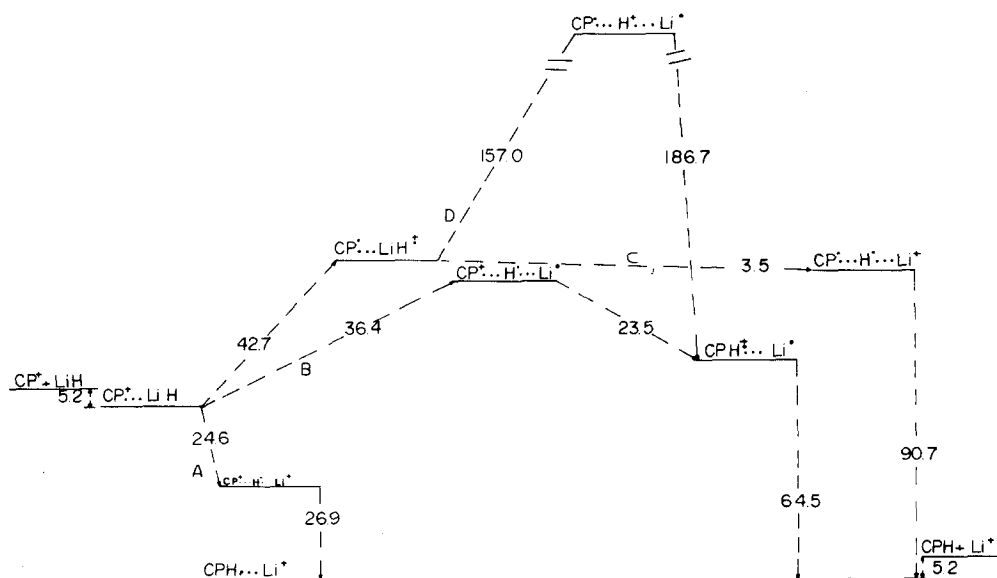


FIG. 1. Energy diagram illustrating the possible channels for $CP^+/CPH/LiH/Li^+$ redox reaction. The relative energies are given in kcal/mol. Positive and negative energies are represented with upward and downward arrows, respectively. The total energy of the reactants at infinite distance has been taken as zero energy. The electrostatic energy has been calculated as indicated in Sec. II. The atomic polarizabilities used are (in atomic units): $C = 8.77$, $H = 2.83$, $Li = 4.0$, $Li^+ = 0.06$, $H = 7.64$. The value for carbon and hydrogen have been taken from Vogel [see Ref. 13(c)]; For lithium ion and atom and for the hydride ion we have carried out an uncoupled HF (sum over states) calculation. The TS has been arbitrarily taken at $R/2 = 2 \text{ \AA}$. The relative orientation mimicks the disposition in LADH complexes (Ref. 1).

electronic energies, and effective charges of the molecular fragments involved in the mechanistic pathways are given in Table I. The atomic polarizabilities have been taken from Vogel's tables.¹³ Those which were not available have been calculated in the uncoupled HF scheme. Since the polarization forces play a complementary role in determining the energy differences, the precise value of the polarizabilities is not very important.

Figure 1 clearly shows that from all possible channels the hydride ion mechanism emerges as the most probable way of transferring two electrons and a proton in this model reaction. The hydride-ion mechanism is in cascade while all other pathways are likely to be found on energy hypersurfaces corresponding to the electronic excited states of the supermolecule. The multipolar complex $CP^+ \cdots H^- \cdots Li^+$ has an energy 24.6 kcal/mol lower than the reactant pair; note that the hydride ion has been put at the middle of the bridge in a perpendicular arrangement.

For the channel B one calculates an energy barrier of 36.4 kcal/mol when an hydrogen atom is put at the middle of the bridge. The subsequent hydrogen transfer leads to a complex between $CPH^+(^2B_1)$ and $Li^+(^2S)$ which is 12.9 kcal/mol above the initial interacting reactant complex. The electron transfer does not require any barrier according to the present scheme.

On the contrary, for channels C and D the electron transfer from LiH towards CP displays a barrier of 42.7 kcal/mol. Thereafter, channel C continues without any apparent barrier. The channel D, however, requires an energy barrier too big to be considered a realistic pathway for this reaction.

B. Energy hypersurface: Adiabatic results

The energy hypersurface contains all the information required for describing the electronic pathway. The hyper-

surface for the ground electronic state has been explored following the conjugated gradient directions after each optimization step.

The R -axis reorientation along the calculated pathway is schematically shown in Fig. 2(b). The corresponding section of the hypersurface (not shown) displays only one true minimum. This is characterized by a molecular complex between the product species, namely Li^+ and CPH [Fig. 2(c)]. The reactive channel has no activation barrier, which is the result suggested by the adiabatic calculation. The electronic structure and geometry of the species appearing on this pathway are not examined with the help of some minimum-energy (ME) profiles related to this barrier-free channel.

1. Intermolecular ME path

The intermolecular parameter R is the $Li-C_1$ interatomic distance. This axis has only the freedom to reorient with respect to the CP^+ plane. Thus for a given R all remaining internal geometrical parameters of the supermolecule are optimized. The results are summarized in Table II.

The ME path has a plateau-like zone for R ranging from 4.0 to 3.8 \AA , and a deep minimum at $R = 2.324 \text{ \AA}$. The nuclear arrangement characteristic of the reactants changes drastically into the product's geometry at $R = 3.775 \text{ \AA}$. The sudden change of the potential energy is, of course, due to the fact that R is not a proper reaction coordinate.²²

The structure at the deep minimum [Fig. 2(c)] will be referred to as interacting product complex (IPC). While the generic structure on the energy plateau will be referred to as interacting reactant complex (IRC).

For the IRC, Mulliken population analysis shows that the $Li-H$ bond polarization increases by 50% with respect to the value found for free LiH. The effective negative charge at the H nucleus is now -0.42 . The intermolecular charge

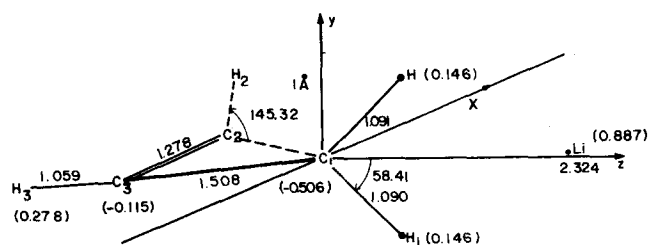
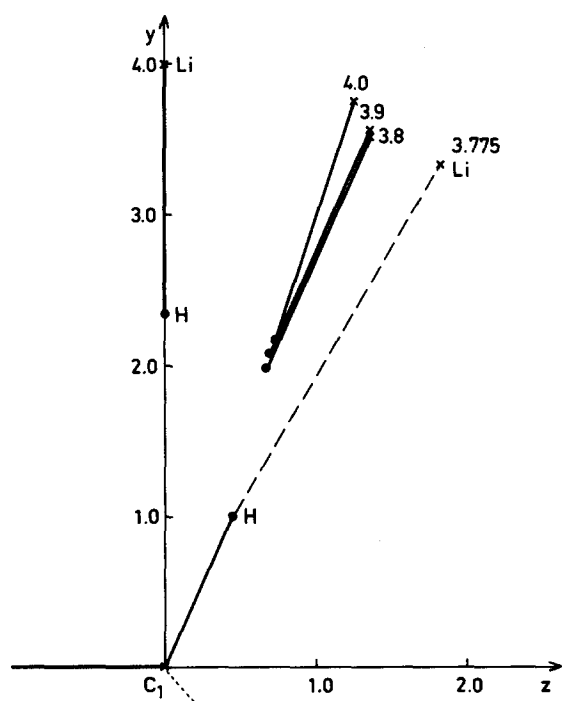
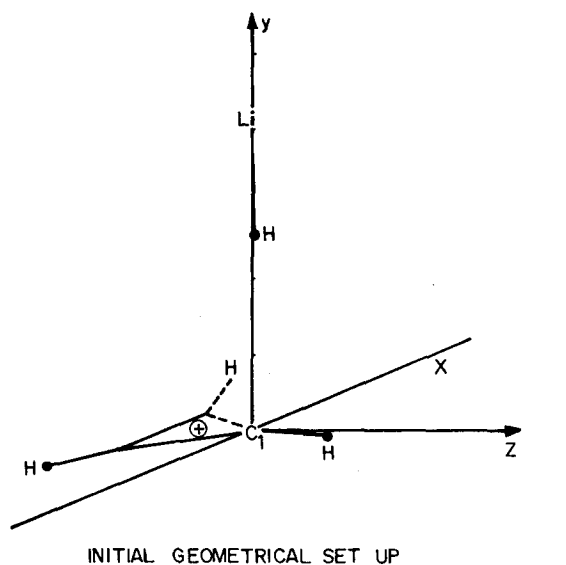


FIG. 2. Schematic view of the structures for constrained $\text{LiCl}=\text{R}$ distances. Indicated in (a) is the initial set up of LiH along the y axis and the final orientation for $R = 4.0, 3.9, 3.8,$ and 3.775 , (b). In the range $4.0\text{--}3.8$ the lithium hydride structure is conserved, while at 3.775 there is no longer a local minimum in the vicinity normal equilibrium distance for LiH , the hydrogen and two electrons are found to be forming a perturbed cyclopropane structure, (c). Distances in Å. Angles in deg. Net atomic charges in a.u.

transfer is small (Table II). Its direction is from the hydrogen donor to the acceptor. The internal geometry of CP^+ is fairly sensitive to the interaction. Furthermore a transformation of the canonical MOs to Boy's localized orbitals²³ shows no orbital interactions between the transferred H_4 and C_1 , nor between the transferred H_4 and lithium. In fact, the localized orbital of "highest" energy has an amplitude only at the position of the hydrogen atom in the bridge. This feature characterizes an hydride ion in the bridge.

The $\text{IPC}(^1A')$ presents a different character in so far as bond polarization is concerned. The overall geometry framework has a C_{2v} symmetry. Although the lithium cation produces a charge displacement from the ethylenic region towards C_1 , no trace of a hydride ion is found in the electronic structure of this complex.

2. Hydride minimum-energy path

A global hydride transfer minimum-energy profile can be obtained by using the $\text{C}_1\text{--H}$ interatomic distance as the control coordinate.²⁴ Total energy, local geometrical changes, effective charges on the hydride donor-acceptor centers, bond orders reduced to atoms C_1 and H and Li and H are reported as a function of the $\text{C}_1\text{--H}$ distance in Table III. In Fig. 3 local geometrical changes and effective charges are depicted as a function of the $\text{C}_1\text{--H}$ distance.

The stretching of the $\text{C}_1\text{--H}$ beyond the equilibrium distance in the IPC (~ 1.10 Å) is associated with an increase of the electron population leading to a negatively charged center at the hydrogen nucleus. Concomitantly, an angle dependent force acts on the lithium cation that drives it upwards from the CPH plane [cf. Figs. 3(a) and 3(b)]. The stretching of the $\text{C}_1\text{--H}$ bond from 1.10 to 1.3 Å leads to a negative effective charge on the transferred hydrogen nucleus and produces $\sim 51^\circ$ rotation of the $\text{C}_1\text{--Li}$ axis. Beyond a distance of 2 Å from the C_1 center the attractive force of lithium on the hydride becomes dominant and this ends up in another local minimum. Note that the geometrical parameters and bond indices of the ring are continuously changing along the hydride reaction pathway (Table III).

C. Electronic mechanism in the supermolecule framework

The supermolecule results described above agree with the diabatic results. They give support to the hypothesis that all along the reaction pathway there is an actual hydride-ion transfer in the ground electronic state. According to the diabatic results the alternative electronic mechanisms are to be found on the excited electronic states hypersurfaces of the supermolecule. A pointwise calculation on the triplet electronic state hypersurface confirms this presumption as will be shown in the next section.

In the protein's active sites the substrates are constrained into a perpendicular arrangement by protein-substrate interactions. It is interesting to focus the attention now on this special situation.

TABLE II. Selected points on the energy hypersurface. The changes in effective charges and typical geometric parameters are indicated.

$d_{\text{Li-C}_1}$	$-E$ (a.u.)	$d_{\text{Li-H}_4}$	$d_{\text{C}_1-\text{H}_4}$	Q_{LiH_4}	Q_{ring}	Q_{H_4}	$d_{\text{C}_2-\text{C}_3}$
4.0	122.833 170	1.6990	2.3045	+ 0.087	+ 0.913	- 0.429	1.3442
3.9	122.833 626	1.7077	2.1960	+ 0.115	+ 0.884	- 0.426	1.3405
3.8	122.834 351	1.7663	2.0363	+ 0.180	+ 0.819	- 0.411	1.3327
3.775	122.884 650	2.6826	1.0988	+ 0.036	+ 0.086	0.086	1.2835
2.324	122.895 938	1.9838	1.0908	+ 0.112	+ 0.146	+ 0.146	1.2777

V. PERPENDICULAR CONSTRAINED ATTACK: ADIABATIC STUDY

A. Intermolecular potential

The intermolecular potential in the ground electronic state for the perpendicular attack of LiH to the CP^+ plane has been calculated. This potential describes not a reaction path but the stability of the partner molecules towards disproportionation into the particles that can potentially be exchanged between them.

The shape of the potential shows three stationary points, two local minima separated by a maximum. The plateau found on the ME profiles above has become a local minimum at $R = 4.3 \text{ \AA}$. A small activation barrier of $\sim 2 \text{ kcal/mol}$ separates the wells in the ground state.

The perpendicular IRC ($^1A'$) [see Fig. 4(a)] contains three strongly charged partners: cyclopropenyl + 0.98, hydrogen - 0.44, lithium + 0.46.

For the ground state there is a maximum on the energy profile at $R = 3.6 \text{ \AA}$. Two negative eigenvalues (- 0.17 and - 0.02) result from diagonalizing the symmetrized force constant matrix. The topography of the hypersurface corresponds to a ridge with one direction characterized by the eigenvalue - 0.02 having a flat shape. The constraints force the system to go over a ridge into the valley where a lower minimum is located.

The perpendicular IRC in the triplet state ($^3A''$) [Fig. 4(b)] displays an intermolecular electron transfer. The LiH fragment acquires a structure similar to $\text{LiH} (^2\Sigma^+)$, while a radical doublet similar to $\text{CP} (^2A_1)$ is found on the other partner. Geometrical relaxation is associated with a large energy drop. The relative orientation of the Li-H vector has changed, it points toward the ring at variance with the orientation found for the ground state.

The (constrained) minimum corresponding to the perpendicular IPC ($^1A'$) [Fig. 4(c)] has nearly the same energy as

the true C_{2v} minimum. The electronic distribution is however fairly different as it will be shown later on.

B. Hydride pathway

The energy profiles on the singlet and first triplet electronic states for the displacement of the hydrogen nucleus in the perpendicular disposition are presented in Fig. 5. The Li nucleus is kept fixed at 4.3 \AA from the Cl center. This is the equilibrium distance of the perpendicular IRC.

The potential energy curves for both states have a double well. The activation energy is relatively large, namely 15 kcal/mol in both profiles. As it will be shown later on, correlation effects do not affect the shape of this curve. The shape reflects the bond breaking and forming process. In the ground state the electronic population credits for a hydride ion as the species which is transferred. In the triplet state a hydrogen atom is found along the pathway.

The geometry and effective charges for the energy minimized structures are summarized in Figs. 4(a) and 4(d) for the ground state.

The hypersurface index associated with the maxima in the reaction profiles differ sensibly: the triplet corresponds to a saddle point, whereas there is a ridge for the ground state.

The interesting facts in this constrained potential are the appearance of a barrier, which can be modulated by intermolecular distance R , the presence of the elusive hydride ion in the ground state profile and, for the triplet state, the $e^- - \text{H}$ mechanism along the exothermic direction.

C. Orienting effects and susceptible bond polarization

Strong orientational effects have been found associated with the C_1 center. In fact, the spatial disposition of the donor and acceptor centers (Li, C_1) together with the disposition of the transferred hydride corresponds to an endo (par-

TABLE III. Total energy and molecular parameters as a function of the Cl-transferred hydrogen (H4) distance. Q : stands for the effective charge; P : indicates the atom-atom bond index; d : signals out the distance in \AA . The entries in Figs. 3(a) and 3(b) completes the description.

$d_{\text{C}_1-\text{H}_4}$	$-E$ (a.u.)	$d_{\text{C}_1-\text{Li}}$	$d_{\text{C}_2-\text{C}_3}$	$d_{\text{Li-H}_4}$	Q_{H_4}	Q_{Li}	$P_{\text{C}_1-\text{H}_4}$	$P_{\text{Li-H}_4}$	Q_{C_1}
1.5	122.859 530	3.2653	1.2996	1.7788	- 0.242	0.822	0.189	0.126	- 0.129
1.6	122.851 304	3.3468	1.3056	1.7578	- 0.288	0.780	0.161	0.156	- 0.085
1.7	122.844 848	3.4291	1.3122	1.7384	- 0.328	0.735	0.132	0.186	- 0.047
1.8	122.840 187	3.5137	1.3188	1.7218	- 0.362	0.688	0.105	0.215	- 0.017
1.9	122.837 116	3.6005	1.3254	1.7076	- 0.388	0.642	0.079	0.242	0.004
2.0	122.835 280	3.6899	1.3312	1.6963	- 0.407	0.601	0.058	0.265	0.016

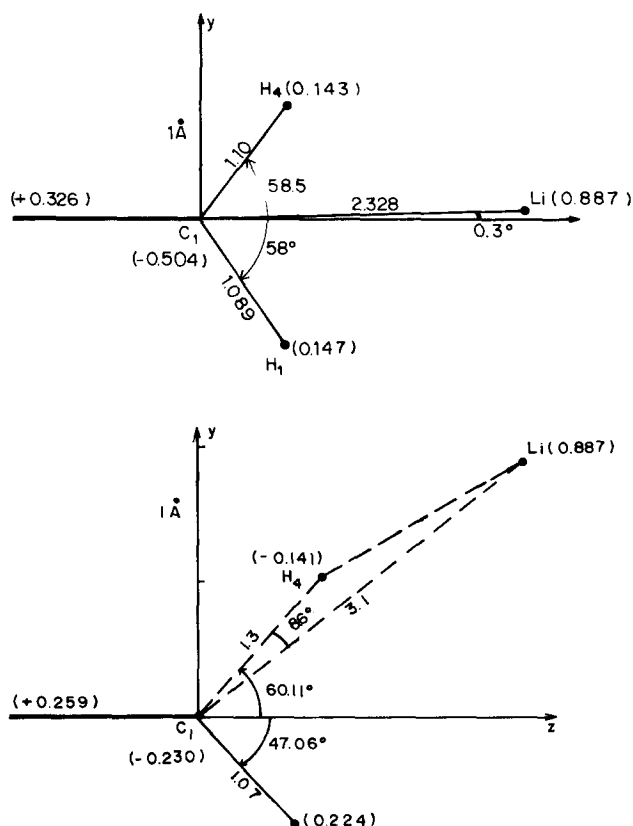


FIG. 3. Schematic view of the geometrical and electronic charges that are taking place at Cl center when the Cl-H bond is being stepwise stretched. The effective charges are indicated in parenthesis, the ring's ethylenic part is reported as fragment. All the remaining geometrical parameters are optimized until the average gradient length is taken below 1×10^{-4} mdyn or mdy $\text{\AA}/\text{rad}$.

allel) arrangement. The interaction is extremely dependent on the internal geometry of the ring. The intermolecular charge transfer is very small. Note that calculations with frozen ring geometry did not show a minimum of this kind.¹⁷

A comparison of the electronic structure of the Cs perpendicular complex and the C_{2v} minimum IPC(1A_1) [cf. Fig. 2(c)] is interesting as it reveals the changes in the electronic distribution produced by reorienting the R axis.

In both geometrical arrangements, there is a shift of -0.134 charge units from the ethylenic-like fragment towards the Cl center. It is only the perpendicular arrangement which shows an appreciable displacement of -0.121 charge units in the direction of the lithium. Since in IPC(1A_1) [Fig. 4(c)] the Li-H distance is similar to the one found for the IRC(1A_1) (Fig. 4(a)) one can consider the hydrogen atom to be shared by both Li and C_1 centers. However no covalent bond can be identified between lithium and the hydrogen atom by using Boy's localization.

The charge displacement is produced by the lithium cation even if it is kept upwards at 4.1 \AA [Fig. 4(d)]. There it can be seen that the hydrogen pointing towards lithium has a nearly zero effective charge while the hydrogen found in the opposite direction displays a fairly large $+0.2$ effective charge. These results suggest that the perpendicular lithium position helps form a hydride-like structure. The results pre-

sented in Sec. III B for the C-H stretching supports this contention. This behavior can be rationalized in simple terms if one uses a valence bond description of the MO results.

Let $\psi_1(\text{C}^-\text{H}^+)$, $\psi_2(\text{C}^-\text{H}^+)$, and $\psi_3(\text{C}^+\text{H}^-)$ be the basic states to describe the electronic structure of the C-H bond. An MO calculation can always be thought of as particular linear combinations of these basis functions. For carboxylic acids the C-H bond breaks down into a proton and a carbanion-like center. In this case the ionic form at equilibrium distance $\psi_2(\text{C}^-\text{H}^+)$ has an energy lower than the $\psi_1(\text{C}^-\text{H}^+)$ and $\psi_3(\text{C}^+\text{H}^-)$. The effect of an electric field on the relative energy of the ionic states can easily be assessed. In a sufficiently strong electric field having a direction favoring the $\psi_3(\text{C}^+\text{H}^-)$ basic state the energy ordering with respect to the $\psi_2(\text{C}^-\text{H}^+)$ state can be inverted. If this latter situation is met one would expect the formation of an hydride ion. Thus, for the C_{2v} IPC [Fig. 2(c)] the effect of the lithium cation is small due to the geometric disposition of Li with respect to the methylene group. While in the perpendicular Cs IPC [Figs. 5(a) and 5(c)] as well as the structures described in Figs. 3(a) and 3(b) the C-H bond shows an increasing weight of the $\psi_3(\text{C}^+\text{H}^-)$ basis function. This behavior is elicited by the Mulliken population analysis.

VI. BASIS SET AND CORRELATION EFFECTS

To which extent the results found with the 4-31G basis set are reliable is a delicate matter to assess. On energetic grounds, Scheiner and co-workers²⁵ have noted the surprisingly good agreement between the results by Roos *et al.*²⁶ using a very large basis set and extensive CI expansion and those with the much smaller 4-31G basis set at the Hartree-Fock level for the system $(\text{HOHOH})^-$. Unfortunately this is not a contention of general validity as our studies on proton transfer in C acids have shown.²⁷ We observe that from the energetic viewpoint the situation herein studied may not be a favorable one: The hydride transfer occurs between two electron-deficient centers $\text{D}-\ddot{\text{H}}-\text{A}$, while proton transfer takes place between two electron rich centers $\text{A}:-\text{H}^+:-\text{B}$.²⁸ Therefore, correlation effects are bound to be important.

The hydride ion is perhaps a unique example where electron correlation plays a significant role in determining its ground electronic structure. Loosely speaking, the electronic structure can be depicted as the mixing of a swollen helium atom with a polarized hydrogen atom carrying an extra electron¹⁴ (this latter is a typical correlation description). Only the swollen helium atom feature can be described with RHF schemes, and this only if appropriate atomic orbitals are included. It is interesting to note that the charge distribution of the hydride ion, as it is obtained with Hylleraas-Kinoshita correlated wave functions, looks much more spatially diffuse than the one for the helium atom.^{14,15} It is obvious that a minimal basis set can hardly represent such an electronic feature of the hydride ion. To include these correlation effects large angular momentum basis functions are required to ensure not only in-out correlation but, most importantly, angular correlations.^{15,29} Unfortunately, such improvements will increase the computing size thereby preventing the study of more complex models.

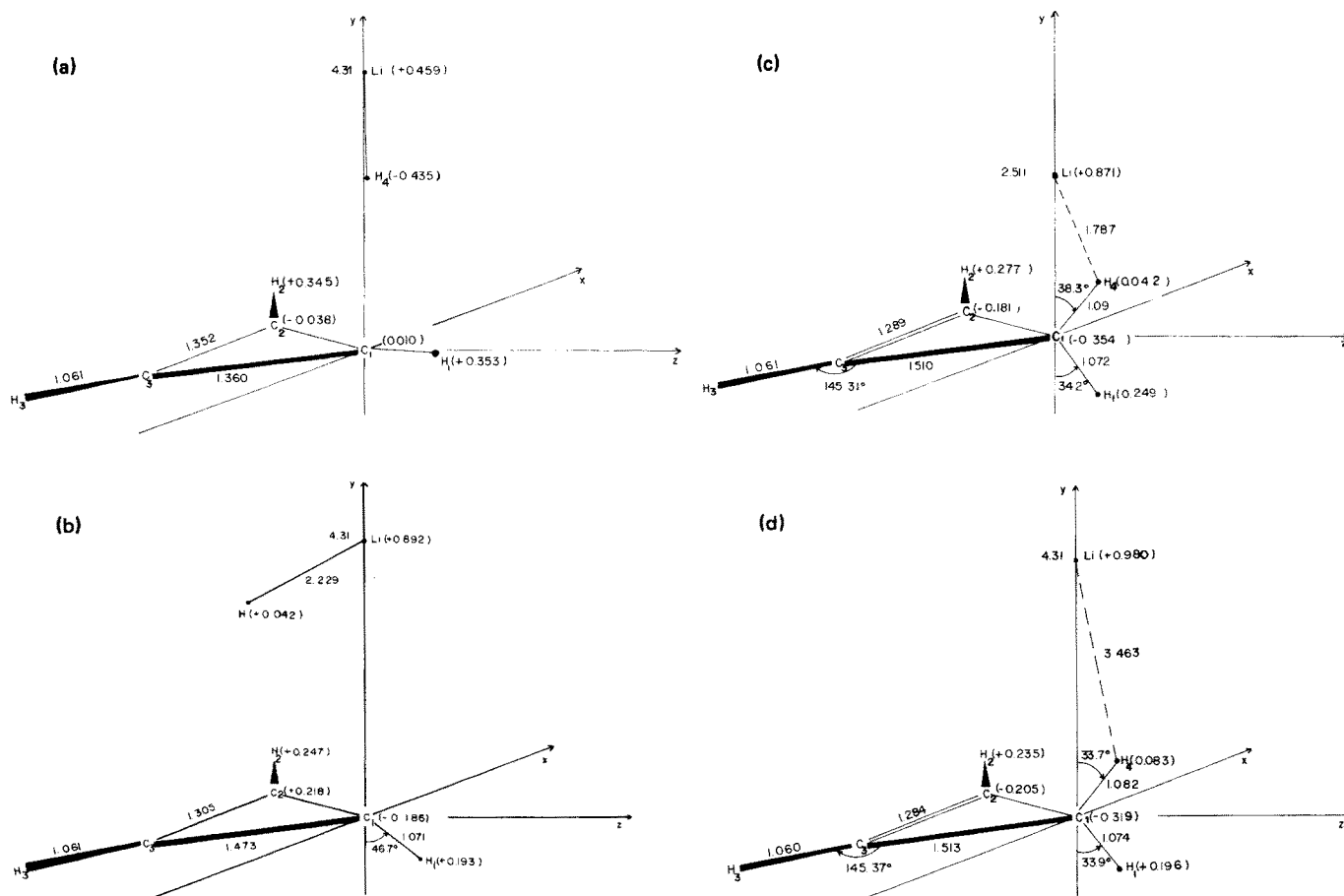


FIG. 4. Equilibrium geometries and effective charges for the molecular complexes characterized with analytical gradient methods for the constrained perpendicular configuration. (a) Reactants in the ground state; (b) reactants in the triplet state; (c) product in the ground state: all parameters are optimized, only Li is constrained on a perpendicular disposition; (d) product in the ground state but the lithium now is kept at 4.31 Å distance.

The correlation effects can be included partially by a CI calculation. A direct CI calculation³⁰ has been carried out for the stationary points of the hydride transfer potential at $R = 4.31$ Å. 22 active molecular orbitals have been included (10 virtual orbitals and 12 occupied orbitals); 7381 configurations result. Table IV summarizes the results.

In absolute value the correlation effects are larger for the species having a hydride ion in the structure. The energy barriers are quantitatively changed but the qualitative and semiquantitative features found at the RHF SCF level are confirmed by these direct CI calculations. Actually, the coefficient of the RHF-SCF determinant in the final wave function is always larger than 0.97. The electronic distribution picture is not going to be much changed by this type of correlation effects.

The discussion above suggests that inclusion of diffuse orbitals³¹ in the basis set should improve the description of an hydride-like structure. Preliminary calculations for the perpendicular IRC and IPC³² with a 3-21 + G basis set confirm these expectations: for the IRC, the effective charge on the incumbent hydrogen grows to -0.78 charge units. Moreover, evidence of a hydride ion was found by us for methanolate and CP^+ in a similar geometric arrangement bridge. These results tend to support the idea of a hydride bond where the particle cementing the molecular association

between two electron deficient centers is a hydride ion. Such a qualitative picture was suggested by Swain *et al.* based on a study of substituent effects on isotope effects to distinguish between proton and hydride transfer.^{28(b)}

VII. DISCUSSION

Electronic aspects of the hydride transfer mechanism for the LiH/CP^+ hydride donor-acceptor model compound have been characterized with *ab initio* RHF and UHF MO SCF calculations. A 4-31G basis set was used for representing the atomic orbitals. Electronic mechanistic pathways have been examined first by studying the corresponding asymptotic dissociation channels, and thereby calculating the electrostatic energy required to assemble the interacting complexes. This procedure leads to a hydride ion transfer mechanism. The supermolecule calculations confirmed this contention. Besides, on the pathway for the perpendicular attack on a cyclopropenyl cation by lithium hydride two molecular complexes have been characterized. The more stable one (IPC) corresponds to a molecular complex between the lithium cation and cyclopropene. The second structure, IRC, corresponds to a highly polarized molecular association where a hydride ion appears to mediate the interaction between the positively charged centers of cyclopro-

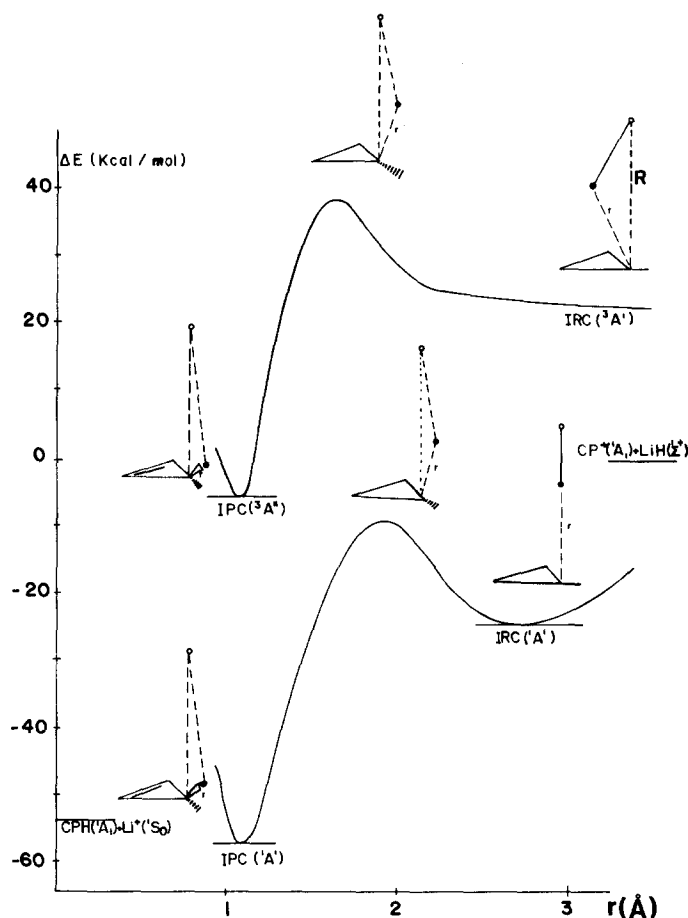


FIG. 5. Hydride transfer minimum energy profile (perpendicular arrangement); the R distance is kept fixed at 4.1 Å; the control coordinate is $r = \text{C-H}$ distance. The lower curve describes the ground electronic state, while the upper curve represents the triplet state. The hydride is represented by a black dot, the lithium is represented with an unfilled circle.

penyl and lithium cations. In the triplet state the pathway from reactants (LiH/CP^+) a two step mechanism is found: an electron transfer is followed by a hydrogen atom translocation.

Direct CI calculations have shown that the RHF picture is basically sound. The present work documents, theoretically, the existence of an hydride-ion bond which was earlier suggested by Swain.^{28b} In the 1982 Faraday Discussions, Newton suggested that the valence structures advanced by Kreevoy to describe molecular associations between pairs of hydride donor-acceptor molecules were reminiscent of the three-center, two-electron bonding associated with the BHB bridges in diborane and other boron hydrides.⁶ We have calculated B_2H_6 with the 4-31G basis set and optimized the equilibrium geometry. The bridge hydrogen atoms there do not have a charge excess which characterize the hydride bond. The structures proposed by Kreevoy⁶ might well be described as a hydride type of interaction. Further theoretical studies are needed to document this type of interaction in more complex systems.

The polarization effect of Li^+ on the C-H bond at the C1 center in cyclopropene has also been confirmed by us in a calculation of 1,2-dihydropyridine and Li^+ . The results sug-

TABLE IV. Direct configuration interaction results for the stationary points of the hydride transfer potential energy curve; the intermolecular distance $R = 4.311$ Å. Self-consistent field energy (E_{scf}) and correlation energy (E_{corr}) in atomic units; C_0 is the coefficient of the SCF-determinant obtained after direct configuration interaction; 7381 configurations have been generated from the 12 occupied and 10 virtual orbitals retained in the present calculations. The interaction energies (ΔE_x) are reported in kcal/mol.

	IRC	TS	IPC
- E_{scf}	122.828 331	122.803 079	122.881 077
- E_{corr}	0.046 285	0.040 833	0.029 035
C_0	0.979 4	0.973 8	0.980 5
ΔE_{scf}	0	15.8	- 33.1
ΔE_{tot}	0	19.1	- 21.8

gest a rationale for one of the roles the catalytic zinc may have in LADH. In the alcohol oxidation step the deprotonation of the alcohol group is instrumental in producing the right C-H polarization; the hydroxyl group bound to the zinc performs such deprotonation.¹ On the other hand, for the reduction of aldehydes or ketones, besides binding the substrate, the zinc electric field may help in polarizing the C-H susceptible bond at the C4 center. The mechanism of Parker and Holbrook for lactate dehydrogenase¹ is consistent with this view also. Moreover, for dihydrofolate reductase the polarization hypothesis provides a rationale for the special disposition of three carbonyl groups in the active site of this enzyme.³³ The negative ends of the carbonyl oxygens are roughly on the opposite side of the hydride transfer. Their electric fields may then help activate the formation of an hydride ion there.

We can conclude that the 4-31G basis set provides a "minimal basis" for representing the hydride electronic features, and, as our calculations on more complex model systems are showing,^{29(a)} the use of the diabatic scheme in conjunction with this basis set offers a method for displaying the energetics of all electronic pathways for realistic model systems.

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