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Nonlocal Density Functional Theory as a Practical Tool in Calculations on Transition States and Activation Energies. Applications to Elementary Reaction Steps in Organic Chemistry

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Abstract: Nonlocal density functional theory (NL) has been evaluated as a practical tool for theoretical studies of organic reactions. Calculations on the two abstraction reactions A ($^{\bullet}CH_3 + CH_4 \rightarrow CH_4 + {}^{\bullet}CH_3$) and B ($^{\bullet}CH_3 + CH_3Cl \rightarrow CH_4 + {}^{\bullet}CH_2Cl$) afforded the activation energies A = 11.7 kcal/mol and B = 8.5 kcal/mol, which compare favorably with the experimental activation energies of 14.1 kcal/mol for A and 9.4 kcal/mol for B. The local density approximation (LDA), without nonlocal correction, afforded a qualitative incorrect description of the two processes with a double-well reaction profile and too small barriers of 1.9 kcal/mol for A and −2.1 kcal/mol for B. Nonlocal (NL) calculations on the dissociation process C ($H_2CO \rightarrow H_2 + CO$) afforded barrier and transition-state structures in close agreement with the best estimate from ab initio calculations. The NL barrier of 75 kcal/mol differs only slightly from the LDA estimate of 74 kcal/mol, and nonlocal corrections are not important for this type of reaction. Nonlocal calculations on the isomerization reactions D ($CH_3CN \rightarrow CNCH_3$) gave an activation energy of 37.5 kcal/mol, which is close to the experimental value of 38.5 kcal/mol. Studies were also carried out on the isomerization processes D′ ($HCN \rightarrow CNH$) and E ($HOC^+ \rightarrow HCO^+$) for which experimental estimates are unavailable. The calculated barriers were 27.6 kcal/mol for D′ and 26.0 kcal/mol for E. The nonlocal corrections were of minor importance for the reactions D, D′, and E. It is concluded that nonlocal density functional theory provides the same accuracy in kinetic studies as the highest level of ab initio theory applied to the reactions A to E.

I. Introduction

The development of powerful optimization techniques based on energy gradient methods has made it possible to routinely carry out a full structural determination of stable molecules (reactants,products) by ab initio methods.[1,2] These energy gradient techniques rely, in general, on an analytical evaluation of the first order of energy derivatives with respect to the nuclear coordinates.[3] A recent extension to the second order of energy derivatives[4] makes it further possible to calculate vibrational frequencies.[4] The Hartree–Fock method seems to afford reasonable geometrical parameters for molecules involving main-group elements, whereas the frequencies calculated by the HF method for the same type of molecules in general are too large.[2] Thus, in the latter case one must resort to ab initio methods including electron correlations or scaling factors. In transition-metal complexes,[5] the electron correlation must be taken into account in determining both structures and frequencies.

One of the exciting newer developments[6] based on energy gradients is undoubtedly the emergence of methods that can provide a perspective on reaction mechanisms. Such methods can be used to determine structures related to the transition state[7a] and afford, in addition, estimates of the reaction energy profile[7b] and activation barrier. The application of ab initio methods to kinetic problems has indicated that the HF method overestimates activation barriers. The application of ab initio methods in which electron correlation is taken into account provides, on the other hand, barriers in good agreement with experiments.[7] However, the high computational cost of correlated ab initio methods restricts their usefulness to rather small systems.

Much interest has lately been given to methods[8] based on density functional theory[9] (DFT) as an alternative to ab initio schemes in the kind of studies mentioned above. This interest was initially motivated by computational expedience, since the time required in DFT methods increases as N^3 with the number of electrons, N, as opposed to N^3–N^4 (HF) or N^5–N^7 (HF + electron correlation) for ab initio schemes. DFT-based methods are thus ideally suited for large size systems. Particular use has been made of the Hartree–Fock–Slater (HFS) Scheme[10] as well as of the local density approximation,[11] of which at least[9c] the LDA method includes electron correlation. Both schemes are referred to as local, since the exchange (HFS) or the exchange and correlation energies (LDA) are expressed approximately as a function of the electron density.

We have recently explored the HFS and LDA methods as tools for determining molecular structures[12] and vibrational frequencies.[13] Our investigation, which is based on an algorithm for the evaluation of energy gradients due to Versluis and Ziegler,[12] has shown that the local methods offer geometrical parameters in better accord with experimental data than are the results from HF calculations, in particular among transition-metal complexes. It appears, further, that the local methods avoid[13] the overesti-

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mation of vibrational frequencies often encountered in HF calculations. Similar conclusions have also been reached by others[8] with regard to local calculations on structures[14] and frequencies.[15] However, the extensive use of the HFS and LDA schemes has revealed a number of shortcomings of the local methods, in particular with regard to the calculation of bond energies, which are systematically overestimated.[8]

Langreth and Mehl,[16] Becke,[17-19] Perdew,[20b,c] Wilson and Levy,[20d] and Lee et al.,[20e] as well as DePristo and Kress,[20a] have in a series of pioneering papers eliminated many of the shortcomings of the local approach by introducing correction terms based on electron density gradients. Correction terms dependent on the Laplacian of the density have also been suggested by Tschinke and Ziegler.[9c] The nonlocal correction terms greatly improve the calculation of atomic exchange and correlation energies[17-19] and afford, in addition, bond energies far superior to those obtained by local methods.[17-19,21,22] Becke[21] has recently in a seminal paper shown that nonlocal methods afford bond energies of the same quality as Pople's G2 method[23] based on ab initio techniques. The nonlocal method has been implemented at the self-consistent level[24] and applied to molecular structures[25] as well as to IR studies on main-group molecules[26] and transition-metal complexes.[27] It was demonstrated[25] that nonlocal corrections greatly improve the accuracy of metal–ligand and metal–metal bond distances.

The objective of the present study is to apply the nonlocal DFT method to calculations on transition-state structures and reaction barriers and compare the results to those obtained by ab initio techniques and experiment. Such a kinetic study will combine energetics with structure determination and frequency calculations and will thus constitute a stringent test of DFT-based methods.

We have previously[28c] implemented an algorithm for optimizing transition-state structures within the HFS-LCAO AMOL program system[29] and applied it to a number of organic isomerization reactions within the HFS scheme. Our study demonstrated that the transition-state structures and the reaction barriers were appropriately reproduced by the HFS method for those reactions. However, the investigation was based on a local scheme and restricted to symmetry-allowed reactions on the singlet surface. Thus, open-shell systems and systems with high barriers and strong interactions between electron configurations have not yet been studied. It is the purpose of the present study to assess the density functional theory in studies of such systems. We shall investigate the hydrogen abstraction reactions A and B

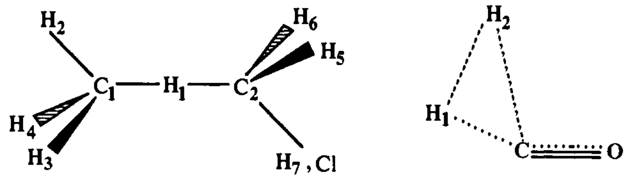

Figure 1. Illustrations of the transition states for reactions A and B (left) and for reaction C (right).

$$^{\bullet}CH_3 + CH_4 \rightarrow CH_4 + {}^{\bullet}CH_3 \tag{A}$$

$$^{\bullet}CH_3 + CH_3Cl \rightarrow CH_4 + {}^{\bullet}CH_2Cl \tag{B}$$

as well as the dissociation reaction C

$$H_2CO \rightarrow H_2(^1\Sigma_g^+) + CO(^1\Sigma^+) \tag{C}$$

and the migration reactions D and E

$$RCN \rightarrow CNR \qquad R = H,CH_3 \tag{D}$$

$$HOC^+ \rightarrow HCO^+ \tag{E}$$

The energy barriers for A and B have been determined by experiments.[30] The energy barrier for C has not been measured directly by experiments but is well established from indirect experimental evidence.[31a,c] The processes D and E have been included here for comparison to previous local calculations.[28]

We shall apply the local density approximation (LDA)[32] as well as the nonlocal corrections (NL)[20c,33] to study reactions A–E. The comparison of transition-state structures and energy barriers obtained by the DLA and the NL should provide information about the importance of the nonlocal corrections to different kinds of reaction systems.

II. Computational Method

The calculations in this study were based on the AMOL program system.[29] The calculations are carried out at two levels of density functional theory. The first level is the local density approximation (LDA)[10] in the parameterization by Vosko et al.,[32] and the second level is a more sophisticated approach in which we have included the nonlocal correlation correction by Perdew[20c] and the nonlocal exchange correction due to Becke.[33] The inner-shell orbitals are kept frozen[29] in the calculations, and the valence electrons are described by a double-ζ plus polarization set of Slater-type orbitals.[34] The numerical integrations involved in our calculation are carried out by the scheme proposed by Boerrigter et al.[34c] Unrestricted SCF are performed for the open-shell systems involved in the reactions A and B. The restricted SCF procedure is applied to the other systems. Geometry optimizations were based on analytical energy gradients evaluated according to the scheme by Versluis and Ziegler.[12] This scheme has been extended to include nonlocal corrections by Fan and Ziegler.[25] The time required to evaluate the energy gradients amounts to 20% of an energy calculation.[12] The accuracy of the

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Table I. Optimized geometries of the Species Involved in the Reaction $CH_3 + CH_3R$ (R = H, Cl)[a]

species		parameter	LDA	NL	ab initio
CH_3Cl	C_{3v}	R_{C-Cl}	1.784	1.804	1.7848[b]
		R_{C-H}	1.101	1.099	1.0872
		α_{HCCl}	108.6	107.5	108.4
CH_4	T_d	R_{C-H}	1.101	1.092	1.084
CH_3	D_{3h}	R_{C-H}	1.092	1.092	1.0734[c]
CH_2Cl	C_s	R_{C-Cl}	1.691	1.720	1.7173[b]
		R_{C-H}	1.090	1.089	1.0750
		α_{HCCl}	117.6	116.8	116.6
		α_{HCH}	124.6	126.7	122.7
TS(A)	D_{3d}	$R_{C_1-H_1}$	1.334	1.359	1.357[d]
		$R_{C_1-H_2}$	1.100	1.100	1.079
		$\alpha_{H_2C_1H_1}$	104.7	104.7	105.1
TS(B)	C_s	$R_{C_1-H_1}$	1.459	1.394	
		$R_{C_2-H_1}$	1.246	1.326	
		$R_{C_1-H_2}$	1.098	1.099	
		$R_{C_1-H_3}$	1.099	1.010	
		$R_{C_2-H_5}$	1.102	1.100	
		R_{C_2-Cl}	1.757	1.778	
		$\alpha_{C_1H_1C_2}$	180.0	178.9	
		$\alpha_{H_2C_1H_1}$	104.0	105.3	
		$\alpha_{H_3C_1H_1}$	101.1	102.9	
		$\alpha_{H_2C_1H_4}$	115.5	114.3	
		$\alpha_{H_5C_2H_1}$	107.0	107.4	
		$\alpha_{ClC_2H_1}$	107.9	106.2	
		$\alpha_{H_5C_2H_6}$	113.4	115.0	

[a] Angstroms for bond lengths and degrees for bond angles. [b] HF/6-31G** calculation. Reference 35a. [c] MP2/6-31G** calculation. Reference 35a. [d] HF/6-31G calculation. Reference 36b.

energy gradients has been examined previously.[12,24] All nonlocal calculations were carried out self-consistently.[24] The frequencies were calculated by a numerical differentiation of the analytical energy gradients, as described elsewhere.[13,26,27] The transition states were optimized by the algorithm developed by Simons et al.[28a] in the implementation due to Baker.[28b] All optimized transition states has been confirmed by a single negative eigenvalue to the corresponding force constant matrix. The processes A and B were studied on the doublet surfaces. The singlet surfaces were considered for all other processes.

III. Results and Discussion

Hydrogen Abstraction Reactions.[35] Hydrogen abstraction by $^{\bullet}CR_3$ constitutes an important branch of radical reactions. The mechanisms for several reactions in this category have been the subject of both experimental and theoretical investigations. The isodesmic process A as a prototype has been studied by a number of ab initio[36] and semiempirical[37] calculations. Process B has also been examined by ab initio methods recently.[38] The energy barriers calculated by the various ab initio schemes are significantly higher than the corresponding experimental activation energies for both reactions. We present in this section a study of the two reactions based on density functional theory (DFT).

The geometries of the reactants, the products, and the transition states in reactions A and B have been optimized fully by the LDA and the NL schemes. The data are compiled in Table I and compared with ab initio results. The numbering for the atoms in the two transition states, TS(A) and TS(B) of reactions A and B, respectively, is illustrated in Figure 1. The structures optimized by different methods are quite similar. The differences are in most cases within 0.02 Å for bond lengths and 2° for bond angles. The only exception is for the transition state TS(B), for which the LDA method yielded a 0.065-Å longer CH_3Cl-CH_3 distance ($R_{C_1H_1}$) and a 0.06 Å shorter ClH_2C-H distance ($R_{C_2H_1}$) than the NL scheme. This means that LDA predicts a somewhat earlier transition state than NL. It is also interesting to note that the substitution of Cl for a hydrogen atom of CH_4 leads to an earlier transition state, which can be seen by comparing the C_2-H_1 and C_1-H_1 bonds as well as the $H_5C_2H_1$ angles in TS(A) and TS(B).

Table II. Relative Energies of the Species Involved in the Reaction[a] $CH_3 + CH_3R$ (R = H, Cl)

	LDA	NL	UHF	post HF	exptl[b]
$CH_3 + CH_4$	0.0	0.0	0.0	0.0	
TS(A)	2.8	12.6	29.7[c]	19.7[d]	
barrier	1.9[e]	11.7[e]			14.1
$CH_3 + CH_3Cl$	0.0	0.0	0.0	0.0	
$CH_4 + CH_2Cl$	−7.6	−4.8			
TS(B)	−1.3	9.3	28.5[f]	18.7[g]	
barrier	−2.1[e]	8.5[e]			9.4

[a] The unit is kcal/mol. [b] Reference 30. [c] UHF/6-31G calculation. Reference 36b. [d] Single-point CI calculations based on the UHF/6-31G geometries and wave functions. The final result was obtained by extropolation. Reference 36b. [e] Corrected by the zero-point energies. [f] UHF/6-31G* calculation. Reference 38. [g] MP2/6-31G* calculation at the UHF/6-31G* geometries. Reference 38.

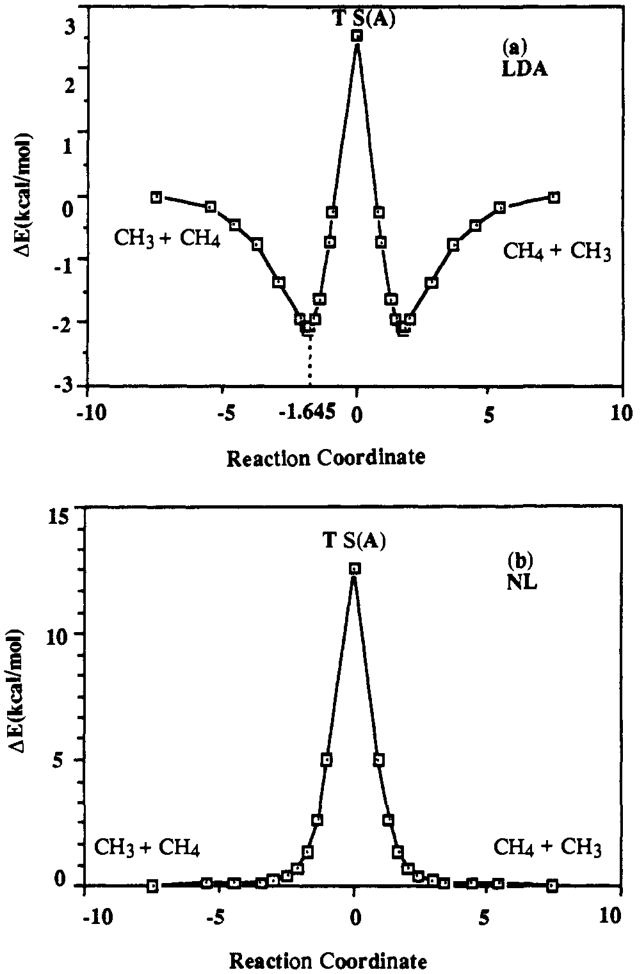

Figure 2. Energy profiles for the reaction $CH_3 + CH_4 \rightarrow CH_4 + CH_3$. The reaction coordinate is taken as $-\Delta R_{C_1H_1}$ before reaching TS(A) and $\Delta R_{C_2H_1}$ after passing TS(A).

The activation energy for reaction A has been determined experimentally[30] to be 14.1 kcal/mol. The Hartree–Fock calculations[36] all yielded much too high energy barriers. We have quoted the results of Sana et al.[36b] in Table II. The energy gap between TS(A) and $CH_4 + CH_3$ is 29.7 kcal/mol according to

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Table III. Vibrational Frequncies of the Species Involved in the Reaction $CH_3 + CH_3R$ (R = H, Cl)[a]

species		LDA			exptl/ab initio[b]		
CH_4	A_1	3308			3137		
	E	1463			1567		
	T_2	1223	3166		1357	3158	
CH_3Cl	A_1	707	1336	3048	732	1355	2966
	E	989	1409	3142	1015	1455	3042
CH_3	A_1'	3080					
	A_2''	686			612		
	E_1'	1310	3307		1385	3150	
CH_2Cl	A'	909	1371	3136			
	A'	971	3303				
	A''	390					
TS(A)	A_{1g}	538	1049	3107	489	1278	2458^i
	A_{1u}	104			38		
	A_{2u}	608*i*	1116	3059	*c*	1330	3243
	E_{1g}	648	1316	3184	785	1584	3380
	E_{1u}	301	1240	1353	374	1501	1604
		3185			3382		
TS(B)	A'	375*i*	113	497			
		582	802	1027			
		1170	1311	1337			
		1363	3065	3107			
		3203					
	A''	61	287	584			
		1012	1307	1329			
		3185	3241				

[a] The unit is cm^{-1}. [b] Experimental data for CH_4, CH_3Cl, and CH_3 are taken from refs 35b, 35c, and 35d, respectively. The frequencies of TS(A) are UHF/6-31G results of ref 36b. [c] Not given in ref 36b.

UHF/6-31G, which is more than double the experimental activation energy. Approximate CI calculations,[36b] on the other hand, yielded a lower barrier of 19.7 kcal/mol.

According to the LDA scheme, the energy of TS(A) is above the energy of $CH_4 + CH_3$ by 2.8 kcal/mol, which is much lower than the experimental value of 14.1 kcal/mol. The energy of $CH_4 + CH_3$ was obtained by considering it as a supermolecule with the separation of $10a_0$ for the $CH_3H–CH_3$ distance. We note further that reaction A takes place through a double-well mechanism on the LDA potential energy surface, as shown in Figure 2a. The surface was obtained by changing the $CH_3H–CH_3$ distance while optimizing all other degrees of freedom. The energy of the reaction system decreases as the CH_3 radical approaches CH_4, until a minimum is reached at the distance of about $4.165a_0$. The minimum is 2.1 kcal/mol below the energy of the two separated reactants $CH_4 + CH_3$.

It is well known[8a] that the local density approximation favors bonding among atoms. Thus, bond dissociation energies calculated by LDA are always much higher than experimental estimates. Therefore, one has reason to suspect that the shallow minimum and the double-well profile predicted by the LDA scheme are artifacts of the local density approximation. Indeed, the minima disappeared on the potential energy surface obtained by incorporating the nonlocal correction. Figure 2b illustrates the energy profile on the nonlocal energy surface. The energy barrier predicted by the NL scheme is 12.6 kcal/mol, which is in good agreement with the experimental activation energy of 14.1 kcal/mol.

Of course, a more reasonable comparison between experiment and theory should include the zero-point vibrational energy correction to the calculated electronic activation barrier. Table III summarizes the vibrational frequencies of the reactants, the products, and the transition states for reactions A and B. We have used the zero-point energy corrections due to the LDA scheme in both LDA and NL calculations. Frequencies estimated by the two methods are usually quite similar,[26] and zero-point energy corrections estimated by the LDA and NL schemes should be within 0.5 kcal/mol of each other. The frequencies of TS(B) obtained by HF/6-31G calculations[36b] are also listed in Table III for comparison. Not surprisingly, the HF frequencies are, in general, higher than the corresponding LDA estimates.[13,26] A noticeable discrepancy between LDA and HF is observed for the imaginary frequency. The HF value of 2458*i* is much higher than the LDA estimate of 608*i*. Furthermore, the imaginary mode was assigned to A_{1g} in ref 36b. We calculated the frequencies by symmetry coordinates, and the symmetry of the imaginary mode is undoubtedly A_{2u}. A simplified depiction of the A_{1g} and A_{2u} modes is illustrated in Figure 3. It is clear from the chemical intuition that the transition mode is more likely to be of A_{2u} symmetry.

Figure 3. Schematic representation of the normal modes A_{1g} (left) and A_{2u} (right) of TS(A).

As indicated in Table II, the energy barrier after the zero-point correction for reaction A is 11.7 kcal/mol according to the NL method, which agrees fairly well with the experimental estimate of 14.1 kcal/mol. The barrier on the LDA potential energy surface is even lower after the correction with a value of 1.9 kcal/mol.

Also included in Table II are the relative energies for reaction B. The LDA method predicts a negative energy barrier for the reaction and is thus in conflict with the experimentally observed[30] activation energy of 9.4 kcal/mol. Once again, the energy profile due to the LDA scheme has a double-well shape. We optimized the geometries of the two minima and the results are shown in Figures 4a and 4c. The structure of the transition state is shown in Figure 4b. The geometries of both minima are very similar to the geometries of the corresponding reactants or products. Figure 5 demonstrates the relative energies of the species involved in reaction B. The minimum for $CH_3–CH_3Cl$ lies below the separate CH_3 and CH_3Cl species by 2.9 kcal/mol.

The nonlocal corrections succeeded again for reaction B. The energy gap calculated by NL is 9.3 kcal/mol, which is in close agreement with the experimental barrier of 9.4 kcal/mol. As in the case of reaction A, the "intermediates" disappeared on the nonlocal potential energy surface as shown in Figure 5. After the zero-point energy correction, the energy barrier is 8.5 kcal/mol. Chen et al.[38] calculated the energy barrier by ab initio methods. Their results are also included in Table II for comparison. The energy barrier predicted by UHF/6-31G* is 28.5 kcal/mol, which is 4 times higher than the experimental barrier. A higher level of ab initio theory, MP2//UHF/6-31G*, reduces the barrier to 18.7 kcal/mol, but this value is still too high by a factor of 2.

We may conclude that nonlocal density functional methods afford an adequate description of the two radical abstraction reactions studied here. The nonlocal corrections due to Becke[33] and Perdew[20c] are essential for an accurate depiction of the reaction

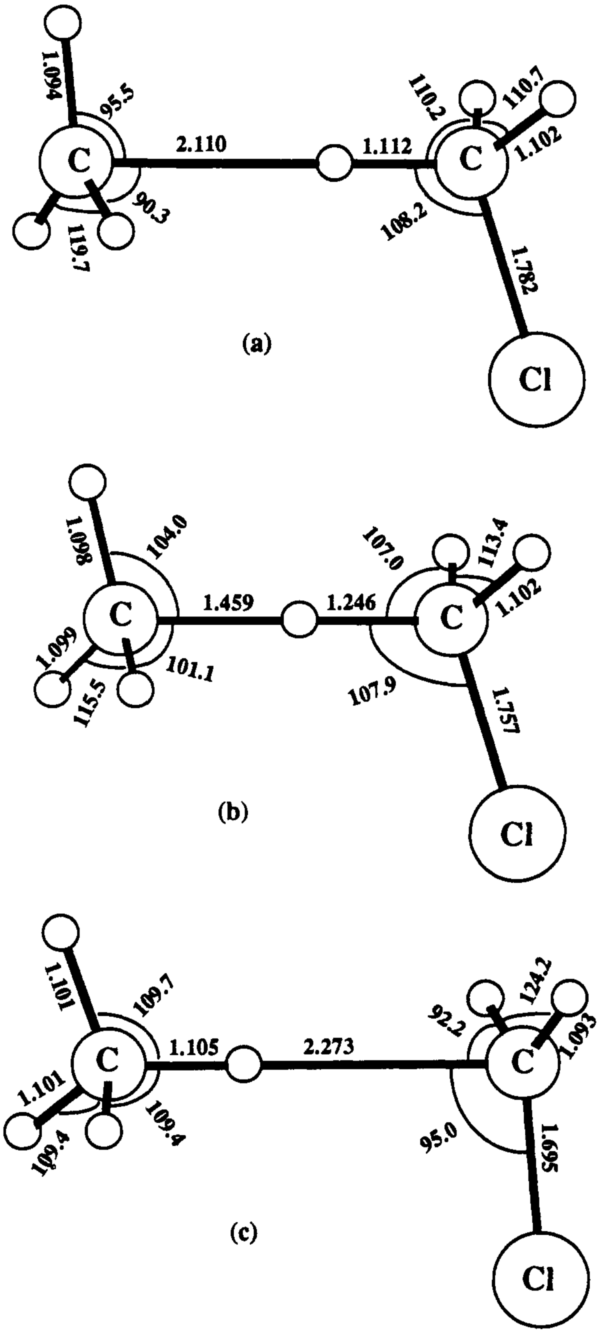

Figure 4. Spurious intermediates a and c and transition state b from LDA calculations on the reaction CH_3 + CH_3Cl → CH_4 + CH_2Cl.

profile and barrier. On the other hand, the local density approximation seems to be inappropriate. It provides a qualitatively incorrect double-well reaction profile with a much too low activation barrier. We expect the conclusion reached here, with respect to the importance of nonlocal corrections, to be valid for all types of reactions with a transition state involving a three-center three-electron bond.

Dissociation Reaction. The photodissociation of formaldehyde has been the subject of extensive experimental[31] and theoretical[39] studies. The dissociation products $H_2(^1\Sigma_g{}^+)$ and $CO(^1\Sigma^+)$ were observed at an energy close to the first singlet excited state (80.6 kcal/mol) of formaldehyde. The dissociation process C is virtually thermoneutral,[31] and the activation energy of the ground-state potential is thus believed[31] to be near the first singlet excitation threshold of 80.6 kcal/mol. However, the early theoretical calculations[39a,b] by Jaffe et al., with a minimum basis set plus CI calculation, gave an energy barrier as high as 112 kcal/mol. Goddard et al.,[39c,d] Dupius et al.,[39g] and Adams et al.,[39h] studied the basis set and electron correlation effects on the energy barrier and found that the calculated barrier decreases considerably when a larger basis set and a higher level of theoretical methods are employed. The dissociation process C is symmetry allowed if the C_s symmetry is retained during the reaction. However, the electron correlation is important during the dissociation process, since the ground state of H_2CO is related to $CO(^1\Pi)$ rather than to $CO(^1\Sigma^+)$, as illustrated in Figure 6. We present here our studies based on density functional theory; both LDA and NL will be employed. Our DFT study on reaction C should reveal whether DFT-based methods are able to handle processes with high barriers characterized by avoided crossings of different electronic configurations, Figure 6.

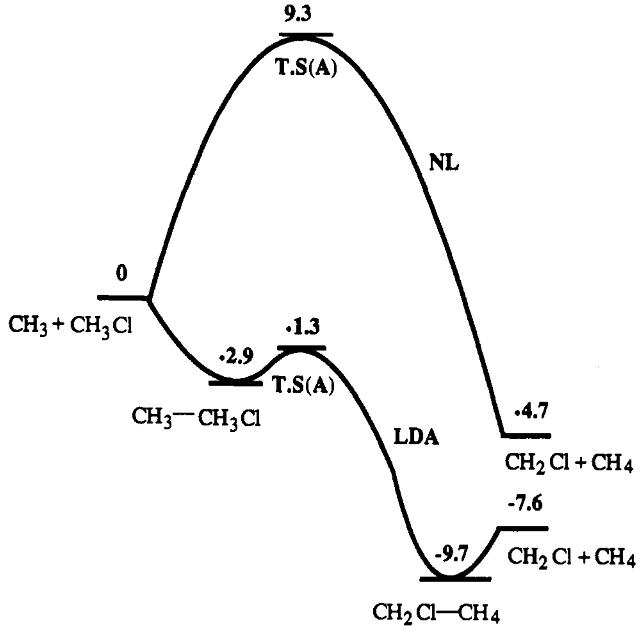

Figure 5. Energy profile (kcal/mol) for the reaction CH_3 + CH_3Cl → CH_4 + CH_2Cl according to LDA and NL calculations.

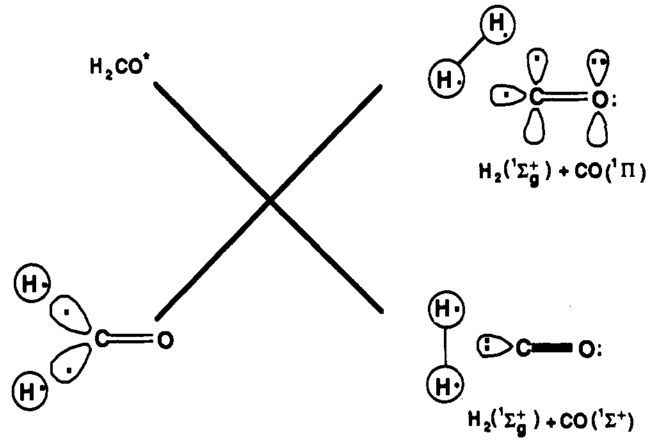

Figure 6. Correlation diagram for the dissociation of H_2CO.

The equilibrium geometry of H_2CO was taken from previous LDA and NL calculations.[25,26] The structural parameters for the transition state in process C are given in Table IV along with the results from ab initio calculations using similar basis sets. The highest theoretical level, MC10(DZDP), in Table IV is close to full CI. It involves CI calculations including single and double

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Table IV. Transition-State Geometry and Reaction Barrier for the Reaction $H_2CO \rightarrow H_2 + CO$[a]

	LDA	NL	HF-(DZP)[b]	SDCI-(DZP)[b]	MC10-(DZP)[c]
R_{C-O}	1.166	1.173	1.151	1.179	1.190
R_{C-H_1}	1.108	1.103	1.104	1.096	1.100
$R_{H_1-H_2}$	1.326	1.355	1.203	1.213	1.371
α_{H_1CO}	163.3	164.6	161.9	161.1	163.7
$\alpha_{CH_1H_2}$	86.8	87.5	86.6	85.7	87.4
ΔE	78.7	79.7	105.9	98.1	89.5
barrier[d]	74.0	75.0	100.2	92.8	84.4

[a] Angstroms for bond lengths, degrees for bond angles, and kcal/mol for energies. [b] Reference 39d. [c] Reference 39g. 10-electron, 10-orbital MCSCF plus CI calculation. [d] Corrected by the zero-point energies.

Table V. Vibrational Frequencies of the Transition State for the Reaction $H_2CO \rightarrow H_2 + CO$[a]

	LDA	HF(DZP)[b]	SDCI(DZP)[b]	MC10(DZP)[c]
A′	3080	3243	3263	3207
	1906	2092	1939	1815
	1347	1526	1555	1282
	779	829	876	791
	1758*i*	2305*i*	2124*i*	1853*i*
A″	877	1024	950[d]	849

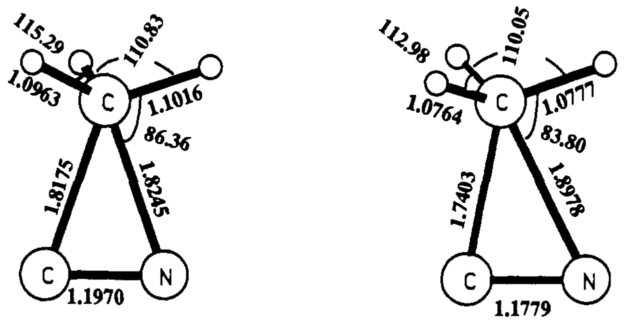
[a] The unit is cm^{-1}. [b] Reference 39d. [c] Reference 39g. 10-electron, 10-orbital MCSCF plus CI calculation. [d] Estimated value.

excitations from the valence orbitals of the MCSCF configurations, which are in turn obtained by ten-electron, ten-orbital MCSCF calculations.[39g] The LDA and the NL predicted similar transition-state structures as shown in Table IV, and both predictions are close to the structure obtained by MC10(DZP). However, a significant discrepancy among different calculations is observed for the H–H distance. SDCI(DZP) predicted a 0.16-Å shorter H–H distance than MC10(DZP), and our results are closer to those of the later.

The vibrational frequenices of the transition state (TS) for reaction C are calculated by LDA, and the results are compared with the ab initio calculation in Table V. It can be seen that the LDA frequencies are close to those obtained by accurate CI calculations using MC10(DZP). The imaginary frequency calculated by HF(DZP) is 450 cm^{-1} away from the corresponding MC10(DZP) value, while the LDA represents this mode very well, i.e., 1758*i* for LDA compared with 1853*i* for MC10(DZP). The frequencies of H_2CO have been taken from a previous study.[26]

The relative energies of H_2CO and the TS are displayed in Table IV. It is obvious that HF(DZP) overestimates the reaction barrier and the electron correlation has the effect of lowering the barrier. The energy gap between H_2CO and the TS on the most sophisticated CI potential energy surface, MC10(DZP), is 89.5 kcal/mol according to Dupius et al.[39g] This barrier is further reduced to 84.4 kcal/mol by the zero-point energy correction. Dupius et al.[39g] concluded that the basis set error could be ~4.0 kcal/mol and the final barrier should be 80.9 ± 3.0 kcal/mol. The other high level ab initio calculation, MP4(SDTQ)/6-31G**// MP2/6-31* by Frisch et al.,[39f] arrived at a similar conclusion with a suggested extrapolated value of 79.6 kcal/mol. Table IV shows that even SDCI(DZP) is not appropriate enough to reproduce the dissociation barrier. The 92.8 kcal/mol of SDCI(DZP) should be 8–10 kcal/mol higher than the full CI barrier.

As shown in Table IV, the LDA scheme yields a barrier of 78.7 kcal/mol. The nonlocal corrections increase the barrier by 1.0 kcal/mol and yield a value of 79.7 kcal/mol. Corrected by the LDA zero-point energies, the barriers predicted by the LDA and the NL are 74.0 and 75.0 kcal/mol, respectively, Table IV. It is interesting to note that the nonlocal corrections are of minor importance for the dissociation process in C, quite unlike the abstraction reactions A and B. Both the LDA scheme and the NL method seem to predict a slightly lower energy barrier than the value estimated at the highest level of ab initio theory. However, compared with the Hartree–Fock method and even truncated CI, the reliability of density functional theory in studies on dissociation reactions as electronically complicated as the process in C, see Figure 6, is evidently very promising.



(a) NL (b) HF/DZP

(c) NL (d) MBPT

Figure 7. Structures of the transition states CN(H) and CN(CH_3). The units are angstroms for lengths and degrees for angles.

Isomerization Reaction. The two isomerization reactions in D have precipitated much theoretical and experimental interest. Most of the interest in the $CH_3NC \rightarrow CH_3CN$ isomerization reaction is related to whether it follows the RRKM mechanism.[40] The isomerization reaction HNC → HCN has, on the other hand, served as a model system for new computational methods[41,42] of potential use in theoretical studies on reaction mechanisms. We have previously investigated[28c] the two isomerization processes by the local HFS scheme and shall here focus on the way in which nonlocal corrections modifies these results.

The structures of the two transition states optimized by the HFS[28c] and NL methods are compared with the results from ab initio calculations[40–43] in Table VI and Figure 7. The transition-state structures calculated by the NL method are slightly different from those evaluated by CI ab initio methods, as illustrated in Figure 7. In particular, the NL method finds the migratory groups (CH_3, H) almost equidistant between carbon and nitrogen, Figures 7a and 7c, whereas the ab initio methods place the migrating groups closer to the carbon atom, Figures 7b and 7d. It is also interesting to note that the distance between the two migratory groups (CH_3, H) and the carbon and nitrogen terminals are longer for NL than for the local HFS method, Table VI. This trend reflects that nonlocal corrections, in general, weaken bonds between atoms.

The energy barrier for the process $CH_3NC \rightarrow CH_3CN$ has been determined experimentally[44] with high accuracy as 38.4 kcal/mol. The DZP (double-ζ plus polarization) Hartree–Fock calculation[43] affords a much too high value of 48.1 kcal/mol, as shown in Table VII. The HF calculation by Saxe et al.,[40] in which a similar basis set was employed, afforded a barrier of 45.5 kcal/mol, still too

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Table VI. Geometrical Parameters of the Transition States Involved in the RNC → RCN (R = H, CH_3) Isomerization Reactions[a]

TS CN(H) (C_s)					TS CN(CH_3) (C_s)			
parameter	HFS[e]	NL	MBPT[b]	SDCI[c]	parameter	HFS[e]	NL	HF/DZP[d]
$R_{C\equiv N}$	1.185	1.190	1.187	1.181	$R_{C\equiv N}$	1.196	1.197	1.178
R_{N-H}	1.354	1.365	1.430	1.430	R_{C-N}	1.767	1.825	1.898
α_{HNC}	56.8	56.54	51.8	52.2	R_{C-C}	1.764	1.818	1.740
					R_{C-H}	1.106	1.102	1.078
						1.101	1.096	1.076
						1.101	1.096	1.076
					α_{HCH}	114.0	115.3	113.0
						109.3	110.8	110.1
						109.3	110.8	110.1

[a] Angstroms for bond lengths and degrees for angles. [b] MP3/6·31G** results. Reference 41. [c] Reference 42. [d] Reference 40. [e] Reference 28c.

Table VII. Relative Energies for Species Involved in the RNC → RCN (R = H, CH_3) Isomerization Reactions[a]

	HNC	HCN	TS CN(H)
HFS	0.0	-16.5	29.8
LDA	0.0	-14.7	30.5
NL	0.0	-15.5	30.7
HF/6-31G**[b]	0.0	-11.0	39.5
MP3/6-31G**[b]	0.0	-16.0	35.4
SDCI[c]	0.0	-14.6	34.9

	CH_3NC	CH_3CN	TS CN(CH_3)
HFS[g]	0.0	-22.6	42.8
LDA	0.0	-23.1	42.1
NL	0.0	-23.0	39.5
HF/DZP[b]	0.0	-19.2	48.1
MBPT/DZP[b]	0.0	-22.7	45.3
exptl	0.0	-23.7[e]	38.4[f]

[a] The unit is kcal/mol. [b] Reference 41. [c] Reference 42. [d] Reference 43. [e] Reference 45. [f] Reference 44a. [g] Reference 28c.

high compared with the experimental value. Redmon et al.[43] applied the SDQ-MBPT(4) method with a large size CI involving about 10^7 configurations at the geometry optimized by a DZP HF calculation, again the calculated barrier of 45.3 kcal/mol is too high. The barrier calculated by the NL method is 39.5 kcal/mol, as shown in Table VII. Corrected for zero-point energy, the barrier calculated by the NL method becomes 37.5 kcal/mol, which is very close to the experimental value of 38.4 kcal/mol. Redmon et al.[43] estimated the zero-point energy to be 4 kcal/mol and obtained a barrier of 41 kcal/mol. Our zero-point energy correction was based on the theoretical frequencies from the previous local study.[28c] The barrier calculated by the local schemes is 42.8 kcal/mol (HFS) and 42.1 kcal/mol (LDA), Table VII. Zero-point corrections again will reduce these numbers by 2 kcal/mol. Thus, nonlocal corrections introduce a small but important adjustment which brings the calculated barrier into closer agreement with experiment.

The isomerization energies for the process $CH_3NC \rightarrow CH_3CN$, as calculated by the DFT-based methods, are seen from Table VII to be in very good agreement with experiment,[45] i.e., 22.6 kcal/mol (HFS), 23.1 kcal/mol (LDA), and 23.0 kcal/mol (NL), as compared to the experimental value of 23.7 kcal/mol. The zero-point energy correction to the isomerization energy amounts to only about 0.1 kcal/mol due to the similarity in the vibrational modes of the two isomers.

The potential energy surface and the transition state for the reaction HNC → HCN have been studied by a number of authors.[42,46] Gray et al.[47] and Peric et al.[48] studied the reaction rates on the basis of their SDCI potential energy surfaces. The experimental estimates for the exothermicity of the reaction vary from 10.3 to 14.8 kcal/mol according to different authors.[49,50] Maricq et al.[51] suggested an even higher enthalpy gap between the two isomers of 17.2–26.3 kcal/mol. Redmon et al.[46d] studied the basis set and electronic correlation effects on the energy separation and suggested a value of 15 ± 2 kcal/mol. The enthalpy gaps of 16.7 kcal/mol (HFS), 14.7 kcal/mol (LDA), and 15.5 kcal/mol (NL), afforded by the DFT-based methods, are all very close to each other and the value of 15 ± 2 kcal/mol suggested by Redmon et al.[46d]

Table VIII. Structures and Relative Energies for Species Involved in the Reaction $HOC^+ \rightarrow HCO^+$[a]

		LDA	NL	HF[b]	post HF[c]	exptl[d]
HOC^+	R_{C-O}	1.151	1.159	1.142	1.161	
	R_{O-H}	1.034	1.025	0.975	0.989	
	E	0.0	0.0	0.0	0.0	
HCO^+	R_{C-O}	1.104	1.109	1.087	1.110	1.105
	R_{C-H}	1.111	1.106	1.086	1.090	1.086
	E	-43.1	-43.9	-29.3	-36.3	
TS	R_{C-O}	1.145	1.153	1.122	1.150	
	R_{C-H}	1.365	1.361	1.266	1.281	
	R_{O-H}	1.361	1.366	1.436	1.379	
	E[g]	27.2	27.5	54.3	42.8	
	barrier[h]	25.7	26.0[e]	50.8[e]	39.3[f]	

[a] The units are angstroms for bond lengths and kcal/mol for energies. [b] Reference 41. HF/6-31G** calculations. [c] Reference 41. MP3/6·31G** calculations. [d] Reference 52. [e] Corrected by the zero-point energies of LDA. [f] Corrected by the zero-point energies of HF/4·31G. [g] Activation barrier without zero-point energy correction. [h] Activation barrier with zero·point energy correction.

An experimental estimate of the energy barrier for the reaction HNC → HCN is not available. The energy barrier for the reaction is 34.9 kcal/mol according to a SDCI calculation.[42] The barriers calculated by the DFT-based methods after applying the zero-point energy correction are 26.7 kcal/mol (HFS), 27.3 kcal/mol (LDA), and 27.6 kcal/mol (NL), respectively. These are all close to the zero-point energy corrected barrier of 30 kcal/mol obtained by an ab initio calculation[2] at the MP4/6-31G**//6-31G* level of theory. It is evident from our study of the two isomerization reactions in D that DFT provides estimates of reaction enthalpies and activation barriers in close agreement with either experiment or the best-available post-HF calculations. It appears, further, that nonlocal corrections introduce a small but significant improvement for this type of reaction.

The isomerization reaction E is similar to the process HNC → HCN but is included here to cover a reaction involving a charged species. The geometries of the three species including the transition state are optimized by the LDA and the NL schemes. The results are displayed in Table VIII. The experimental data[52] are available only for HCO^+, which are also given

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Table IX. Vibrational Frequencies of the Species Involved in the Reaction $HOC^+ \rightarrow HCO^+$ [a]

		LDA	HF[b]			LDA	HF[b]
HOC^+	σ	3119	3463	HCO^+	σ	3142	3317
	σ	1968	1997		σ	2238	2288
	π	317	620		π	786	1051
TS	A′	2102	2208				
		1896	2056				
		1278*i*					

[a] The unit is cm^{-1}. [b] Reference 41. HF/5-31G//MP3/6-31G** calculations.

in Table VIII. Geometries optimized by the LDA and the NL agree with experiment fairly well. The discrepancies are within 0.005 Å. The geometries for the transition state obtained by the LDA and the NL are similar, but the latter is closer to the MP3/6-31G** geometry, as shown in Table VIII.

Nobes et al.[41] studied the basis set and CI effects on the theoretical energy barriers. The results obtained by different ab initio calculations ranged from 77.0 kcal/mol at the HF/4-31G level to 39.4 kcal/mol for MP3/6-311G***//MP3/6-31G**. The study revealed that a larger basis set and a higher level of theory always decreased the barrier. The value of 42.8 kcal/mol listed in Table VIII was obtained[41] by MP3/6-31G**//MP3/6-31G**. Being corrected by the zero-point energy, the best result that Nobes et al.[41] has obtained is 35.9 kcal/mol. Our calculations by LDA generate a lower barrier of 27.2 kcal/mol. The nonlocal corrections slightly raise this barrier to 27.5 kcal/mol. The influence of the nonlocal corrections to the energy barrier for the isomerization reaction E is thus negligible. The zero-point energy corrected barrier for the NL is 26.0 kcal/mol, which is 9.9 kcal/mol lower than the value of 35.9 kcal/mol obtained by MP3/6-311G***. It is possible that such a discrepancy will be reduced when more extensive CI is included in the ab initio calculations. The vibrational frequencies calculated by the LDA are given in Table XI.

IV. Concluding Remarks

We have studied the hydrogen abstraction reactions A and B. The local density functional theory predicted lower energy barriers than the experimental observations, but the nonlocal corrections successfully rectified the underestimated barriers yielding remarkable agreement with the experiment. The reaction mechanisms proposed by the LDA and NL schemes are qualitatively different, and it is suggested that the double-well reaction profile introduced by LDA with two intermediates is incorrect and is an artifact of the local approximation, which is known to overestimate bonding between atoms. The nonlocal corrections, on the other hand, seem to represent the experimental findings and should be used in studies on reactions involving a transition state with a three-center, three-electron bond.

The dissociation reaction C is appropriately described by the LDA scheme. The influence of the nonlocal corrections is much smaller for reaction C than for either A or B. It is encouraging to see that DFT-based methods are able to handle "symmetry-forbidden" reactions with a high barrier, where interactions between two or more configurations are of importance, Figure 6. More work is needed to understand how DFT-based methods are able to treat this category of processes.

The isomerization reactions D and E are also described well by the DFT-based methods, and the nonlocal approximations provide a small but significant improvement. It can be concluded that the nonlocal method due to Becke[33] and Perdew[20c] demonstrates considerable promise as a practical tool in kinetic studies on organic reactions.

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Catalysis of the Ring-Opening and Isomerization of Cyclopropane by Complexation with Metal Radical Cations: An ab Initio Study

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Abstract: The ring opening and isomerization of cyclopropane are shown by ab initio calculations to be catalyzed by complexation with $Be^{\bullet+}$. The reactions proceed via a common metallacyclobutane radical cation intermediate formed in a reaction that is endothermic by 12.3 kcal mol^{-1} relative to the cyclopropane–$Be^{\bullet+}$ complex. From this intermediate, three alternative reaction paths were examined, two isomerizations to give a propene–$Be^{\bullet+}$ complex and a C–C bond cleavage forming a carbene–ethylene–$Be^{\bullet+}$ species. These reactions are found to be exothermic by 5.4 and 5.2 kcal mol^{-1} relative to the cyclopropane–$Be^{\bullet+}$ complex, respectively. The isomerization of cyclopropane to give propene is calculated to be exothermic by 8.0 kcal mol^{-1} (exptl 7.9 kcal mol^{-1}). Remarkable parallels to transition-metal catalyzed reactions were found for all the reactions examined.

Introduction

The ability of transition-metal complexes to effect structural changes in organic substrates is widespread in organometallic chemistry, examples are the metal-assisted rearrangements of strained-ring molecules, particularly the reactions of cyclopropanes to olefins, and the metal promoted isomerization of olefins.[1] In this paper we focus our attention on the conversions of cyclopropanes. The related isomerization of olefins will be the subject of further work.

The gas-phase thermal isomerization and ring-opening of cyclopropane require activation energies of 60–61 and 64–65 kcal mol^{-1}, respectively.[2] Yamaguchi et al.[3a] and Getty et al.[3b] found

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