Journal of the American Chemical Society / 101:10 / May 9, 1979

Ab Initio Mechanistic Study of Radical Reactions. Transition States and Reaction Barriers for the Reaction of Atomic Hydrogen with Acetylene

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Received July 11, 1978

Abstract: Ab initio molecular orbital methods have been applied to the addition and abstraction reactions $CH{\equiv}CH + H \rightarrow CH_2{=}\dot{C}H$ and $CH{\equiv}CH + H \rightarrow CH{\equiv}\dot{C} + H_2$. The reaction pathways and geometries for the transition state are investigated within the unrestricted Hartree-Fock SCF theory. The addition reaction proceeds with trans stereochemistry via an "early and loose" transition state, while the abstraction reaction prefers a "late and tight" transition state. The respective barrier heights are calculated to be 6.2 and 32.4 kcal/mol. Both reaction barriers originate primarily from the exchange repulsion interaction and from intramolecular deformation. It is also found that forward and then back charge-transfer interactions occur as the reaction proceeds. The formation and weakening of chemical bonds at the transition states are also discussed.

I. Introduction

Reactions of atoms are among the simplest of chemical processes. They play an essential role in a variety of free-radical reactions and provide us rather favorable conditions for detailed, quantitative treatments.[1] Atom reactions with closed-shell molecules include the processes of "addition" and "abstraction". Abstraction reactions with saturated molecules have been studied extensively by theory and experiment beginning with the simplest reaction $H + H_2$.[2] By contrast, less (especially theoretical) attention has been paid to reactions involving relatively large, unsaturated organic molecules.[3] While much experimental progress has been made for radical addition to olefinic bonds, the reactions with acetylenic compounds seem to be less common and their detailed study is still in early stages.[1,4] Although the number of the comparative studies to date is relatively limited, probably an important conclusion is that carbon-carbon triple bonds are less reactive than double bonds toward free radicals.[1d,4a]

In this paper, we present a theoretical analysis of the addition and abstraction reactions of atomic hydrogen to acetylene in the anticipation that the system may be representative of radical reactions with more complex acetylenic compounds. The reaction of H and C_2H_2 is receiving increasing attention because of its recognized importance in the oxidation, photolysis, radiolysis, and pyrolysis of hydrocarbons.[5] It is also an important step in the photochemically induced reactions occurring in the upper atmosphere of Jupiter.[6] The absolute rate parameters for the addition reaction have been recently measured by several authors,[7-11] using different experimental techniques. Kinetic studies of the abstraction reaction are very limited. Little is known as yet about the potential energy surface for the reaction of H with C_2H_2.

Our primary purpose here is to gain, from a quantum-mechanical point of view, some knowledge of this potential surface, especially reaction barriers and geometries for the transition state. This information should be helpful for dynamical and mechanistic studies of the reaction. Transition-state models,[9c] which have been assumed in order to discuss the rate parameters in terms of RRKM theory, can be tested against the present results

For a deeper understanding and chemical interpretation of the potential surface, the reaction barrier, ΔE, will be expressed as a sum of the intramolecular deformation (DEF) and the intermolecular interaction (INT) energies.[12,13] The former is quite similar to the promotion energy for molecular formation from atoms,[13] and the latter energy consists of the electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT), and their mixing (MIX) terms,[12] each of which has clear physical meaning. The relative importance and roles of these terms will be assessed in relation to the reaction course and the origin of reaction barriers. The same analysis bears on the charge redistributions during the reaction. Our hope is that these analyses will provide a starting point for the understanding of reaction mechanisms from a unified point of view.

All computations reported here are performed within the framework of ab initio unrestricted Hartree-Fock SCF theory, employing a modified version of the GAUSSIAN 70 programming system.[14] While the optimized geometries for the abstraction reaction were searched by the minimal STO-3G basis set,[15] the geometries for the addition reaction were fully optimized with the split-valence 4-31G basis set.[16] All other calculations were performed with the 4-31G basis set. The reaction barriers at the transition state were also calculated using a more flexible basis (triple split-valence 6-311 G basis set[17] with p-type polarization functions on hydrogen atoms).

II. Results and Discussion

Addition Reaction ($CH{\equiv}CH + H \rightarrow CH_2{=}\dot{C}H$). By several preliminary calculations, we learned that a reaction pathway with C_s symmetry is the most favorable. Thus, seven internal coordinates (Figure 1) are required to describe the addition of a hydrogen atom to acetylene. The position of the attacking hydrogen is specified by two parameters, R and γ. The geometrical changes in the acetylene fragment are specified by three bond lengths (r_1, r_2, and r_3) and two bond angles (α and β).

In Figure 2 we schematically show the energy minimum path obtained from $R = 2.6$ Å to the product (vinyl radical). The hydrogen atom initially approaches acetylene with as large an angle as $\gamma = 105°$, and with the progress of the reaction opens away from the carbon-carbon bond. At the same time, the acetylene molecule is geometrically deformed to take a trans configuration. The C-C bond length, r_1, is considerably enlarged by $\Delta r_1 = 0.14$ Å throughout the reaction, while there is only a slight increase in the C-H lengths r_2 and r_3.

The changes in potential energy along the reaction path are shown in Figure 3 as a function of R. The energy first increases gradually (destabilization) with decreasing R, attains a maximum, and then decreases monotonically (stabilization), the addition reaction being exothermic. In order to illustrate the importance of geometrical relaxation during the reaction, it is also shown in Figure 3 how the potential energy changes

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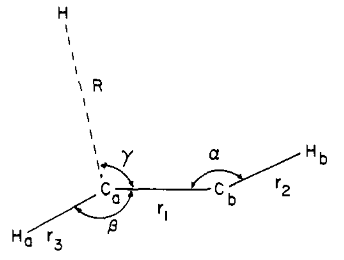


Figure 1. Geometrical parameters and labeling of atoms for the reaction of atomic hydrogen with acetylene.

Table I. Computed Optimized Geometries for Reactant, Transition State, and Product in the Addition Reaction of H and C_2H_2[a]

parameters	reactant[b]	transition state	product
R		1.930	1.078
r_1	1.190 (1.203)	1.224	1.332
r_2	1.051 (1.061)	1.053	1.068
r_3	1.051 (1.061)	1.054	1.074
α	180.0 (180.0)	171.7	135.3
β	180.0 (180.0)	160.5	121.5
γ		109.7	122.2

[a] Bond lengths in angströms and bond angles in degrees using the 4-31G basis set. [b] Values in parentheses are experimental results by E. H. Plyler and E. D. Tidwell, *J. Opt. Soc. Am.*, **53,** 589 (1963); W. J. Lafferty and R. J. Thibault, *J. Mol. Spectrosc.*, **14,** 79 (1964).

Table II. Harmonic Force Constants (K) for Reactant, Transition State, and Product in the Addition Reaction of H and C_2H_2[a]

constants	reactant[b]	transition state	product
K_R		−0.132	5.66
K_{r1}	20.23 (16.86)	13.07	8.83
K_{r2}	7.15 (6.42)	6.99	6.42
K_{r3}	7.15 (6.42)	6.19	6.08
K_α	0.397 (0.248)	0.151	0.541
K_β	0.397 (0.248)	0.276	1.12
K_γ		0.398	1.08

[a] Stretching force constants in mdyn/Å and bending force constants in mdyn Å using the 4-31G basis set. [b] Values in parentheses are experimental results by I. Suzuki and J. Overend, *Spectrochim. Acta, Part A*, **25,** 977 (1969).

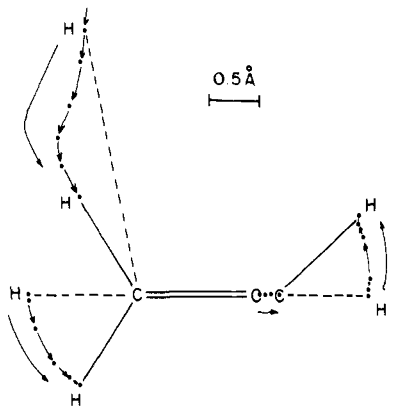


Figure 2. Schematic description of the addition of H to C_2H_2. The arrows indicate the movements of atoms with the progress of the reaction. The dashed lines specify the geometries at an initial stage, while the final product is represented by the full lines.

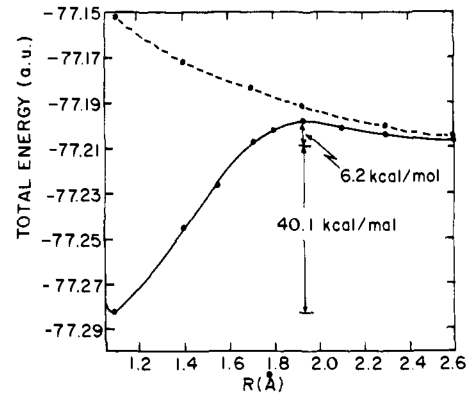


Figure 3. Potential energy curves in the 4-31G basis for the addition of H to C_2H_2 along the reaction pathway as a function of R. The dashed line indicates an approach of H to C_2H_2 without molecular deformations of acetylene.

when the hydrogen atom approaches a frozen acetylene. (Cooperative effects of intermolecular interactions and molecular deformations are discussed below.)

The computed barrier height is found to be 6.2 kcal/mol. This value is not changed significantly by the larger 6-311 G basis set calculation (6.1 kcal/mol). The reaction barriers are in reasonable agreement with recent experimental Arrhenius activation energies:[18] 2.5 kcal/mol over the temperature ranges 243-463 K[10] and 2.4 kcal/mol over 193-400 K.[11] The exothermicity is calculated to be 40.1 kcal/mol, while the experimental value is 41 kcal/mol.[19]

The saddle-point geometry is given in Table I. Over 300 points were calculated to locate the transition state. For comparison purposes, the optimized molecular geometries for the reactant ($CH{\equiv}CH$) and product ($CH_2{=}\dot{C}H$) are also given in this table. It is of interest to note that the transition state for the addition reaction is at a fairly early stage (R = 1.930 Å). This result may be compared to the Hammond postulate,[20] which states that the transition state should resemble closely the reactants in a highly exothermic reaction. However, there are some significant geometrical changes in the acetylene fragment, particularly an extension of the C-C bond and a considerable loss of linearity.[9c] Further, we noted, during the optimization processes, that at the transition state the potential surface is fairly flat with respect to bond angles α and β.

For more detailed information on the potential surface, we give in Table II the diagonal harmonic force constants (K) for the reactant, transition state, and product. Our interest here is how the force constants change with the progress of the reaction, rather than their absolute values. While the changes in K_{r2} and K_{r3} are relatively small, there are larger decreases in the stretching (K_{r1}) and bending (K_α and K_β) force constants at the transition state. These changes in the force constants can be characterized by charge redistributions due to various interactions.

The Mulliken population analyses are given in Table III. As expected, there is a large decrease in the overlap population between carbon atoms. It is noteworthy that at the transition state there is only slight new bonding between the attacking hydrogen (H) and its nearest acetylenic carbon atom (C_a). This suggests that the transition state is "loose", in spite of a considerable weakening of the C-C bond, and that the reaction is electrophilic at this stage, as is obvious from the atomic electron density on the attacking hydrogen (Table III).

Stereochemistry of Addition Reaction. One may argue that there are two stereoisomers (I and II) possible for the hydrogen atom addition to acetylene. Although in this system products are distinguishable only for isotopic differences, such stereochemical considerations are important for a general understanding of the radical addition to substituted acetylenes (see Chart I). In the isomer II the attacking hydrogen atom is cis to the unpaired electron orbital, while I is a trans radical.

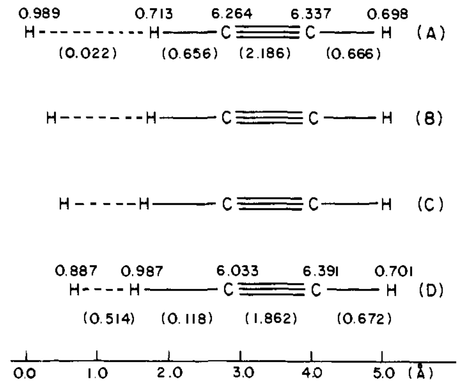
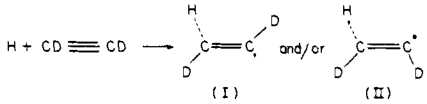


Figure 4. Schematic description of the abstraction reaction of H with C_2H_2 up to the transition state. Atomic electron densities and overlap populations (in parentheses) are given for the path points (A) and (D) in the 4-31G basis set. The potential energies (au) are (A) −76.318 45, (B) −76.311 45, (C) −76.297 25, and (D) −76.297 25.

Chart I



In an attempt to find a possible path for the cis addition and examine energy differences between cis and trans additions, we optimized all geometrical parameters as a function of the reaction coordinate R by using parabolic fits. For large R, we did not find an energy minimum or maximum for a cis configuration. In the region $R < 1.8$ Å, we obtained metastable cis configurations except that significant energy differences between cis and trans additions always favored the latter. For example, at a distance $R = 1.7$ Å, a cis configuration is less stable by 6.8 kcal/mol than is the corresponding trans one. Although more complete studies of the potential surface are indeed needed, it might be conjectured that the trans addition is generally more favorable in a static sense for acetylenic compounds as long as the steric effects of substituents are not severe. In this connection, it is of interest to note that in the experiments with HI and C_2D_2 in an argon matrix at 4.2 K only the trans product is formed.[21]

Abstraction Reaction ($CH{\equiv}CH + H \rightarrow CH{\equiv}\dot{C} + H_2$). The reaction model investigated is an axial abstraction ($\alpha = \beta = \gamma = 180°$ in Figure 1). The representative reaction points obtained along the reaction path are schematically shown in Figure 4. The energy profile in Figure 5 shows that the abstraction of an H atom from acetylene is endothermic by 21.7 kcal/mol. The computed saddle point is at $R - r_3 = 0.865$ Å, $r_1 = 1.209$ Å, $r_2 = 1.067$ Å, and $r_3 = 1.330$ Å. Reflecting the endothermicity, we see that the transition-state geometry is very close to the product. The abstraction reaction therefore gives rise to a tight transition state, as is apparent from the Mulliken atomic and overlap populations given in Figure 4. The transition state is at the electrophilic stage of the reaction.

The calculated reaction barrier of 32.4 kcal/mol is much larger than that of the addition reaction. The larger 6-311 G basis set calculation gives a slightly smaller barrier of 30.6 kcal/mol. To our knowledge, there is only one kinetic datum available for the abstraction reaction. An experimental Arrhenius activation energy measured over the temperature ranges 1000–1700 K is found to be 19.0 kcal/mol.[22] Our calculated reaction barriers may be somewhat too large,[18] owing to the fact that barriers for reactions involving bond breaking tend to be overemphasized in the Hartree–Fock approximation.[25] However, it is evident that the addition reaction is more favorable and faster than abstraction. William and Rowland[23] were able to compare the rate constant for abstraction of an H atom by an F atom from C_2H_2 to the rate constant for F atom addition to C_2H_2; the ratio was found to be about 0.13.

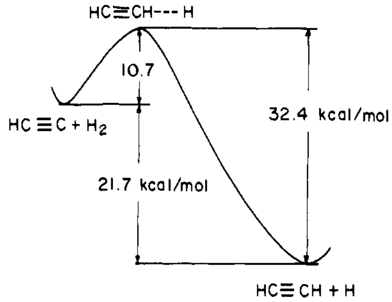


Figure 5. Energy profile for the abstraction reaction of H with C_2H_2 in the 4-31G basis set.

Table III. Gross Atomic and Overlap Populations (P) Associated with Reaction Centers for the Reactant, Transition State, and Product in the Addition Reaction of H and C_2H_2[a]

center	reactant	transition state	product
$P_{C_a\text{-}C_b}$	2.168	1.796	1.023
$P_{C_a\text{-}H}$		0.042	0.760
$P_{C_b\text{-}H}$		−0.023	−0.080
P_{C_a}	6.296	6.280	6.383
P_{C_b}	6.296	6.231	6.140
P_H	1.0	1.033	0.828

[a] For the numbering of the atoms, see Figure 1. Results refer to the 4-31G basis set.

III. Mechanistic Considerations

In this section, we investigate mechanistic features for addition and abstraction reactions in terms of various chemically interpretable energy components for the initial, intermediate, and final stages of the reactions.

Origin of Reaction Barriers and Initial Reaction Course. We first consider the addition reaction and examine the relative importance and roles of various interactions. The calculated energy components at the transition state are given in Table IV, where a negative (positive) value corresponds to stabilization (destabilization). The intermolecular INT energy is a sum of the attractive (−17.1 kcal/mol) and repulsive (19.0 kcal/mol) energies. The attraction is 53% electrostatic (ES), 3% polarization (PL), and 44% charge transfer (CT), while the repulsion is mainly due to exchange (EX). Note that a large destabilization due to EX is overshadowed considerably by the significant contributions of the attractive ES and CT interactions, the net INT interaction being relatively small but repulsive. The contribution of the PL interaction is rather small.

The reaction barrier, ΔE, of 6.2 kcal/mol arises from the intermolecular INT (31%) and intramolecular deformation DEF (69%) energies. The DEF (as well as EX) energy plays a principal role for the source of the reaction barrier at the transition state. If, however, molecular deformations of the acetylene fragment are not permitted at all, the reaction barrier is significantly increased to 9.6 kcal/mol (see also Figure 3). This is ascribable to the increase in the EX repulsion and the decrease in the CT attraction, especially the former effect, as is shown in Table IV. In other words, the geometrical distortions at the transition state take place so as to reduce the destabilization arising from the EX interaction.

In this regard, it is instructive to mention briefly the behavior of the EX interaction along a reaction course up to the transition state. We have already found that the hydrogen atom

Table IV. Energy Component Analysis for the Transition State in the Addition Reaction of H and C_2H_2[a]

	with deformation	without deformation
ES	−9.0	−9.2
EX	18.9	25.9
PL	−0.6	−0.6
CT	−7.5	−6.9
MIX	0.1	0.4
INT[b]	1.9	9.6
DEF	4.3	0.0
ΔE[c]	6.2	9.6

[a] Energies in kcal/mol for the 4-31G basis set. [b] INT = ES + EX + PL + CT + MIX. [c] ΔE = INT + DEF.

Table V. Energy Component Analysis for the Transition State in the Abstraction Reactions[a]

	CH≡CH + H	CH_4 + H[b]
ES	3.0	−10.3
EX	62.4	65.9
PL	−5.3	−5.0
CT	−82.5	−62.1
MIX	30.4	13.3
INT[c]	8.0	1.8
DEF	24.4	22.6
ΔE[d]	32.4	24.4

[a] Energies in kcal/mol for the 4-31G basis set. [b] Reference 13. [c] INT = ES + EX + PL + CT + MIX. [d] ΔE = INT + DEF.

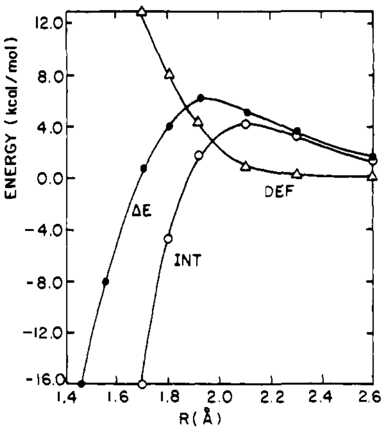


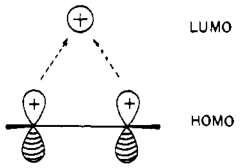
Figure 6. Variations in the energy ΔE (●) and its components INT (○) and DEF (△) along the pathway for the addition of H to C_2H_2 in the 4-31G basis set.

Table VI. Changes in Bond Overlap Population (P) Caused by Various Types of Interactions at the Transition State of Addition and Abstraction Reactions[a,b]

	addition			abstraction	
	old bond	new bonds		old bond	new bond
	C_a-C_b	C_a-H	C_b-H	C_a-H_a	H_a-H
ΔP_{DEF}	−0.086	0.0	0.0	−0.062	0.0
ΔP_{EX}	0.020	−0.136	−0.034	0.076	−0.290
ΔP_{PL}	−0.002	0.0	0.0	0.058	0.0
ΔP_{CT+MIX}	−0.304	0.178	−0.008	−0.622	0.804
total change	−0.372	0.042	−0.046	−0.550	0.514

[a] A positive (negative) value indicates an increase (decrease) in bond overlap population at the transition state with respect to reactant molecules. For the overlap population of reactant, see Table III. The numbering of the atoms is given in Figure 1. Results refer to the 4-31G basis set. [b] The ES interaction does not change the populations.

Chart II



approaches acetylene with rather large angle γ to reach the transition state. This is because the attacking hydrogen would suffer a larger EX repulsion with π electrons in a triple bond, if it chooses a course with a smaller angle γ (a direct attack to a triple bond produces a bridged structure). Note, however, that the CT interaction tends to prefer a course with a smaller angle γ. Up to the transition state, the CT stabilization is dominated by the forward charge transfer from acetylene to the attacking hydrogen, as has been pointed out. With an increase in the angle, γ, the charge transfer interaction is reduced to some extent, as is easily rationalized from the following simple HOMO-LUMO interaction scheme (see Chart II). In fact, these trends are confirmed by the actual calculations. As compared with the change in CT with respect to the angle γ, the corresponding changes in ES and PL are relatively small. Thus, the addition reaction proceeds to the transition state along a path which is least EX repulsive, but with some sacrifice of the CT stabilization. The EX repulsion is further reduced via molecular deformations.

We now proceed to the abstraction reaction. The energy components for the transition state are given in Table V. The DEF and EX energies again play a dominant role for the origin of the reaction barrier. The CT interaction is the main attractive term, while the ES and PL interactions play a minor role. As compared with the results for the addition reaction (Table IV), the absolute values of each energy component are much larger, reflecting a "late and tight" transition state for the abstraction reaction.

In Table V are also given the energy components for the transition state in the hydrogen-abstraction reaction with a saturated hydrocarbon, viz., CH_4. There is a considerable resemblance between both types of abstraction reactions in the magnitude and relative importance of various interactions, except that the ES interaction contributes to destabilization in the abstraction reaction of H and C_2H_2. This is because, at shorter range, the classical electron-nuclear attractive component of ES is canceled out by the electron-electron and nuclear-nuclear repulsive components. At an earlier stage of reaction, however, the former attractive component can outweigh the latter two repulsive components, the ES interaction in general giving net stabilization. For example, the changes in the ES energy (kcal/mol) as a function of R are −0.4 (R = 2.14 Å), −4.6 (R = 2.22 Å), −2.8 (R = 2.48 Å), and −1.2 (R = 2.77 Å) with $\alpha = \beta = \gamma = 180°$. These results suggest that there exists near R = 2.3 Å an energy minimum for the ES interaction.

Bond Formation and Weakening at the Transition State. In Table VI are given the component analyses for the bond overlap populations pertinent to reaction centers. It is clearly shown here how the interchange of chemical bonds takes place at the transition state in terms of the interactions given in Tables IV and V. In both addition and abstraction reactions, old bonds are weakened almost exclusively by the (CT + MIX) interaction, augmented by DEF. The EX interaction rather strengthens the old bonds. For the formation of new bonds, the EX and (CT + MIX) interactions play an important role. New bonds can be formed only when the antibonding contribution of the former is overshadowed by the larger bonding contribution of the latter (note that in the addition reaction the C_b-H bond remains antibonding). The contribution of the PL in-

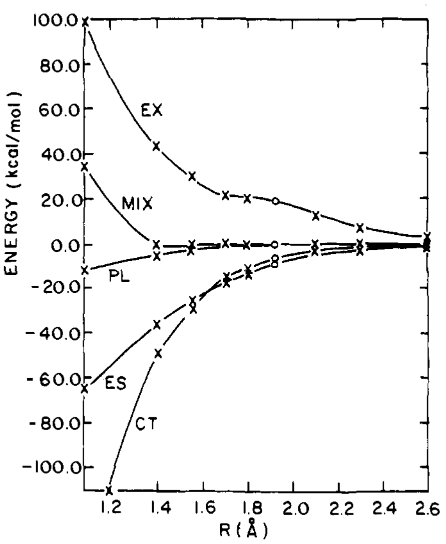


Figure 7. Variations in the energy components of the intermolecular INT energy along the pathway for the addition of H to C_2H_2 in the 4-31G basis set. The circles indicate the values at the transition state.

teraction is small. However, we find that it plays an even more important role when coupled with the CT interaction than when it acts alone.[24]

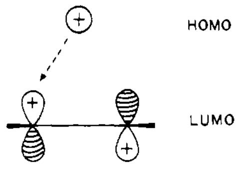
Process from Transition State to Product. We next examine what types of chemical interactions play an important role in proceeding through the transition state to the products. In Figure 6 are shown the variations in the energy, ΔE, and its components, INT and DEF, along the pathway of the addition reaction as a function of R. Essentially the same results were obtained for the abstraction reaction. The trends shown in Figure 6 have been seen also in other reaction systems[13] and are believed to be common to all reactions with a reaction barrier.

At early stages of reaction, it is the INT energy that governs the reaction barrier, ΔE. The barrier height at the transition state is determined by a compromise between the increasing DEF destabilization and INT stabilization. A large increase in the DEF energy in the neighborhood of the transition state is correlated with a significant drop in the INT energy. In other words, molecular deformations occur by changing the effective intermolecular interactions. Noteworthy here is that upon going through the transition state the INT energy is more rapidly decreasing than is the DEF energy increasing, the net energy ΔE turning out to be attractive.

We are now in a position to clarify which energy components are responsible for the rapid decrease in the INT energy. For this purpose, the variations in the energy components of the INT energy are summarized in Figure 7 as a function of R. As the reaction approaches the final stage, the stabilization brought about by the ES, PL, and CT terms completely outweighs the opposing destabilization due to EX and MIX. It is to be noted that the increasing contribution of the EX repulsion is also reduced to a great extent by the molecular deformations. The contributions of the attractive ES and PL interactions may be less important, as compared with CT. The contribution of the CT interaction increases drastically with the progress of the reaction and becomes a dominant attractive term, though it is rather small up to the transition state. Thus, it is the CT interaction that is responsible for a main driving force for the final stage. The same trends are also found for the abstraction reaction.

Further decomposition of the CT term shows that the ratios of forward CT ($C_2H_2 \rightarrow H$) to back CT ($C_2H_2 \leftarrow H$) energies are 1.9 for the transition state (R = 1.930 Å) and 0.6 for the product (R = 1.078 Å) in the addition reaction. This means that the drastic increase in the CT interaction is strongly due to the back charge transfer from H to C_2H_2. This fact is also reflected conveniently in the electron density (P_H) of the attacking hydrogen atom; P_H = 1.033 (R = 1.930 Å), 1.027 (1.85 Å), 1.001 (1.7 Å), 0.907 (1.4 Å), and 0.828 (1.078 Å), suggesting that the final stage is characterized by a nucleophilic reaction.

Chart III



The contribution of the back CT interaction becomes more effective with the increase in the approaching angle γ, as is evident from the following HOMO-LUMO interactions (see Chart III). This suggests another explanation why atomic hydrogen approaches acetylene with rather large angle γ. Similar considerations are also applicable to the fact that in general radicals prefer an axial abstraction to an insertion-like path. Further, the interchange of chemical bonds, i.e., the new pairing and decoupling of opposite spins, takes place smoothly via the successive forward and back charge transfer processes.[26] The importance of the two-way CT interactions (followed by spin polarization)[27] seems to be common to all radical reactions with closed-shell molecules. These general mechanisms will play an essential role in governing the reaction course, orientational effect, and reactivity for free-radical reactions.

IV. Concluding Remarks

To extend our understanding of radical reactions with unsaturated compounds, the addition and abstraction reactions of atomic hydrogen and acetylene were investigated, from a mechanistic point of view, by using ab initio molecular orbital theory.

The addition reaction proceeds with trans stereochemistry and gives rise to an "early and loose" transition state in spite of considerable geometrical and electronic changes in the acetylene fragment. By contrast, the abstraction reaction prefers a "late and tight" transition state characterized by the strong new bond and weak old bond. The reaction barrier of 6.2 kcal/mol for the addition reaction is much smaller than the barrier of 32.4 kcal/mol for the abstraction reaction. The exchange repulsion as well as molecular deformation interactions play essential roles in giving rise to the reaction barriers.[28-40]

In terms of the energy decomposition analysis which we have employed, the successive forward and back charge transfer interactions lead to the origin of stabilization. The importance of the two-way charge-transfer interactions should be emphasized in relation to the reaction course and smooth bond interchange. This effect is also closely related to the avoidance of orbital (or state) crossing.[27a] Thus, the central attacks of radicals to unsaturated centers, resulting in bridged structures, are generally unfavorable[27,40] because the back charge transfer interaction is seriously obstructed, and a large exchange repulsion with π electrons results. The insertion-like approaches to saturated bonds are also inadequate[27,41] for similar reasons, though the forward charge transfer interaction seems to be always permissible. If, however, the back charge transfer interaction is allowed and the exchange repulsion is not severe, the central addition as well as insertion-like reaction would take place. Examples include the addition of Al radical to C_2H_4[42] or the insertion-like approach of H atom to alkali metal dimers.[43]

In the present study, the contributions of the ES and PL interactions are relatively small. In the reactions of polarizable radicals or the reactions with polar substrates, these contributions may be expected to play a more significant role.

By restricting ourselves to the Hartree–Fock approximation, we have implicitly omitted the effects of electron correlation including dispersion terms. A more exact treatment based on the configuration interaction method with sufficiently large basis sets would be very worthwhile. Nevertheless, the results and trends found here are expected to retain their essential validity and offer considerable hope that apparently complex chemical reactions can be interpreted in terms of simple molecular orbital concepts.[44-46]

Acknowledgment. The authors are grateful to Professor K. Morokuma for energy component analysis programs and S.N. is thankful to J. O. Noell for computational consultation. Comments on the manuscript by Dr. J. V. Michael are gratefully acknowledged. The Instruction and Research Computer Center of The Ohio State University provided a grant of computer time.

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