

## POTENTIAL SURFACES FOR SIMPLE REARRANGEMENTS

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Abstract - Quantum mechanical methods for the location and characterization of rearrangement transition structures are reviewed. Activation barriers are shown to be sensitive to the inclusion of polarization basis functions and electron correlation. Applications to vinylidene  $\rightarrow$  acetylene rearrangements are described. The parent species,  $H_2CC$ , rearranges to HCCH without a significant activation barrier. However, significant barriers are found for certain substituted vinylidenes.

### INTRODUCTION

Unimolecular rearrangements are perhaps the simplest examples of reactions that may be studied by theoretical methods. Given that some molecular species is initially in an equilibrium structure, A, the theory should examine paths through which a second structure, B, can be reached. Both A and B will be represented by local minima on the potential surface, the locations characterizing the equilibrium geometries. All paths connecting A and B must pass through regions of energy greater than that of either A or B. Each path must have an energy maximum. The lowest maximum energy for all possible paths is the lowest energy that must be available for the motion,  $A \rightarrow B$ , to occur on the classical potential surface (that is, in the absence of quantum mechanical tunneling). Such an energy will occur at a saddle point or col on the potential surface, normally known as the transition state or transition structure (T) for the reaction.

Several pieces of information about the transition structure are important in discussions of the reaction process. In the first place, the energy of T relative to that of A,

$$E = E(T) - E(A) \quad (1)$$

is the classical activation energy for the forward reaction,  $A \rightarrow B$ . Secondly, harmonic force constants at T give information about effective vibration frequencies for the activation complex, also required for theories of rate constants. These frequencies may be used to compute "zero point energies" at T and when compared with comparably computed zero point energies at A, will give a vibrational correction to the activation energy. Finally, one of the frequencies at T will necessarily be imaginary; this is in the direction of the normal reaction coordinate. The magnitude of this imaginary frequency will relate to tunneling corrections to reaction rates.

All of these features of the transition structure can be studied by *ab initio* molecular orbital theory. In this lecture, we will discuss such methods, illustrating them by applications to vinylidene-acetylene rearrangements.

### QUANTUM MECHANICAL METHODS

The simplest quantum mechanical procedures are of the Hartree-Fock type, using a single molecular orbital configuration and restricting each such orbital to be a linear combination of a set of basis functions. The location of minima and saddle points on a Hartree-Fock potential surface is possible by a variety of techniques, notably aided by the development of methods for obtaining first and second derivatives of the energy with respect to nuclear coordinates (1). The results will depend on the basis set used. In our work, a series of increasingly sophisticated bases are employed: minimal (ST0-3G), split valence (3-21G), split valence + polarization (6-31G\* or 6-31G\*\*) and triple split valence + polarization (6-311G\*\*).

Once the minima and saddle points on the Hartree-Fock surface have been located, it is next necessary to investigate how the resulting relative energies are modified by inclusion of electron correlation. This is most easily done by single point computations at the Hartree-Fock geometries. We have mostly used Møller-Plesset perturbation theory (2-4) to take account of electron correlation. A single computation at third order perturbation theory with the 6-31G\*\* basis would then be denoted by MP3/6-31G\*\*//HF/3-21G if the geometry of the stationary point had previously been determined at the Hartree-Fock 3-21G level.

At second and third order of perturbation theory, only double substitutions of the Hartree-Fock determinant have to be taken into account. At fourth order, single, double, triple, and quadruple substitutions are involved. The triple substitutions, which correspond to three-electron correlation effects, are particularly hard to deal with, and their contributions to the energy lowering has only recently been computable (4). As noted below, they turn out to be important in the determination of activation barriers.

Ideally, the theoretical geometries of equilibrium and transition structures should be re-fined at levels which include electron correlation. This is now possible using second-order Møller-Plesset theory (MP2) or configuration interaction methods; some reaction surfaces have already been explored by such methods.

#### THE VINYLIDENE-ACETYLENE REARRANGEMENT

Vinylidene,  $H_2C=C:$ , is the parent of the unsaturated carbene series,  $R_1R_2C=C:$ , and is one of the simplest systems capable of undergoing rearrangement to the more stable species, acetylene (HCCH). As such, the corresponding singlet potential surface has received much theoretical attention. It provides a useful test case for the comparison and evaluation of various theoretical methods.

Most work has proceeded by assuming  $C_{2v}$  symmetry for vinylidene and then exploring the potential surface to determine a planar transition state,  $HC(H)C$ , on the way to acetylene. Relative energies are summarized in Table 1. The first *ab initio* computation of the transition structure, by Strausz, et al (5), used a small uncontracted  $sp$  basis and gave a very high barrier of 76.7 kcal/mol. However, details of the geometry used were not given. A full *ab initio* determination of the geometry of the transition structure was first carried out by Dykstra and Schaefer (6) using Hartree-Fock theory and a double zeta basis. They found a barrier of 26 kcal/mol; the comparable 3-21G basis gives a similar result. Addition of polarization functions lowers the barrier by about 10 kcal/mol (3,6). This substantial effect is found in many carbon compounds where d-functions lower the energy preferentially in situations of low local symmetry. Next, electron correlation was taken into account and a substantial further lowering of the barrier was found. This occurs both with the Møller-Plesset theory (taken to fourth order in the space of single, double, and quadruple substitutions - MP4SDQ) (3) and with self-consistent electron pair theory (6), closely related to configuration methods. These two studies appeared to give agreement at the time (1978) on an activation barrier of about 8 kcal/mol.

More recent work has indicated that even this value is significantly too large for the barrier to rearrangement (7). This is illustrated by the last four entries in Table 1. Addition of polarization functions on hydrogen lowers the barrier further by about 1 kcal/mol. Refinement of the geometries at the correlated MP2 level makes little change. Next, a further expansion of the basis from a double valence split to a triple split was undertaken (6-31G\*\* to 6-311G\*\*). This leads to an additional energy lowering of the barrier by about 2 kcal/mol. In addition, inclusion of triple substitutions in the fourth order correlation theory (use of full MP4) also leads to a significant reduction in the barrier.

The final estimate for a classical barrier is only 2.2 kcal/mol. These numbers are broadly consistent with those of another recent study by Osamura, Schaefer, Gray, and Miller (8) who obtain 5.4 kcal/mol without including the triple substitution effect. Finally, the classical barrier has to be corrected for zero-point vibrational motion. Using HF/6-31G\* force constants, the zero-point energy is calculated to be smaller in the transition state than in either minimum, giving an effective barrier of only 0.9 kcal/mol. Thus, the very large barrier predicted in the first study has virtually disappeared as the theory has been refined. The final conclusion is that the  $C_{2v}$  vinylidene structure is either a very shallow minimum or itself is a saddle point on the surface. In the latter case, vinylidene would be the transition structure for the experimentally known degenerate rearrangement of acetylene in which the two hydrogens exchange places (9).

#### REARRANGEMENT OF SUBSTITUTED VINYLIDENES

Although there is no direct experimental evidence for the existence of vinylidene, various substituted vinylidenes are believed to have long lifetimes. Thus,  $F_2C=C:$  has been generated in the gas phase (10); the chemistry of  $(CH_3)_2C=C:$  has also been well documented (11). It is therefore of interest to apply similar theoretical methods to these systems.

Table 2 summarizes some recent results. For a singly substituted species,  $XHCC:$ , rearrangement may occur either by shift of X or of H. For  $CH_3HCC:$ , the computations (12) indicate that the barrier for methyl shift is about 22 kcal/mol, much larger than for the hydrogen shift. Indeed, the barrier for H-shift in  $CH_3HCC:$  is substantially lower (by about 6 kcal/mol) than it is in vinylidene itself at the same level of theory. Comparable results have been obtained by Goddard (13) who also examined the dimethyl compound.

Table 1: Relative Energies (kcal/mol)<sup>a</sup> for the C<sub>2</sub>H<sub>2</sub> singlet potential surface.<sup>b</sup>

Level	Vinylidene	Transition Structure	Barrier
HF/Small uncontracted	37.9	114.7	76.7
HF/3-21G//3-21G	38.6	64.3	25.7
DZ	35.7	61.7	26.0
HF/6-31G**//6-31G*	34.2	50.6	16.4
DZ+P	33.5	48.2	14.7
MP4SDQ/6-31G**//6-31G*	42.0	50.1	7.9
SCEP/DZ+P	40.0	48.6	8.6
MP4SDQ/6-31G**//6-31G*	41.7	48.5	6.8
MP4SDQ/6-31G**//MP2/6-31G*	42.4	49.0	6.6
MP4SDQ/6-31G**//MP2/6-31G*	43.1	47.8	4.7
MP4/6-311G**//MP2/6-31G*	45.9	48.1	2.2
Add zero-point-corrections	44.1	45.0	0.9

a. Relative to acetylene.

b. See references 3, 5-8 for details.

Table 2: Relative Energies (kcal/mol)<sup>a</sup> for substituted vinylidene rearrangements

Compound	Path	E(Vinylidene)	E(transition)	Barrier
MeHCC: <sup>b</sup>	Me shift	46.5	68.3	21.8
	H shift		48.4	1.9
FHCC: <sup>c</sup>	F shift	42.6	75.7	33.1
	H shift		41.4	-
F <sub>2</sub> CC: <sup>c</sup>	F shift	25.3	61.6	36.3

a. Relative to the substituted acetylene.

b. MP4SDQ/6-31G\*\*//HF/3-21G without zero-point corrections.

c. MP4SDQ/6-31G\*\*//HF/3-21G with HF/3-21G zero-point corrections.

The results are similar for the fluorovinylidene cases (14). Again, a single F substituent causes the hydrogen shift to occur even more easily than in vinylidene itself. The fluorine shift, on the other hand, requires substantial activation energy. The same is true in difluorovinylidene. The qualitative origin of these high barriers for methyl and fluoro shifts is not yet clear although the antiaromatic character of the cyclic 4  $\pi$  transition structure is likely to be a contributing factor.

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