Potential Energy Surfaces for the Bis-Silylation of Ethylene

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The reaction mechanism for the addition of disilanes to the π bond of ethylene was studied by ab initio molecular orbital methods. Optimized structures were predicted using restricted Hartree−Fock wave functions and a triple ζ plus polarization basis set. The reaction barrier was found to be about 50 kcal/mol using both second- and fourth-order perturbation theory with the same basis set.

I. Introduction

Double silylation of unsaturated organic molecules with disilanes provides a convenient route to bis(silyl) compounds, which can in turn serve as monomers for the synthesis of silicon-containing polymers. Such polymers have an exciting future, for they can be designed to possess thermal stability, transfer optical and electrical information,[1] and exhibit useful mechanical properties as sol−gels, lubricants, and composites.[2]

Experimental studies of bis-silylation, though few in number, suggest that the reaction requires a formidable energy of activation, since transition metal catalysis has been needed to achieve appreciable yields. Hayashi and co-workers[3] discovered that double silylation of ethylene with methylated disilanes proceeds in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes. Okinoshima and co-workers[4] utilized palladium catalysts with bulky ligands to add methyl-substituted disilanes in cis fashion across unsaturated acetylene derivatives. Since then, a variety of other palladium complexes have efficiently catalyzed the double silylation of alkynes with sterically hindered phenyl-substituted disilanes.[5,6] Several instances of metal-catalyzed double silylation of allenic compounds have also been reported.[7,8] Sakurai et al.[9] carried out the double silylation of acetylenes, as well as of 1,3- and 1,2-dienes. However, it was Okinoshima and co-workers[10] who, in 1972, performed the first successful double silylation of 1,3-butadienes in the presence of a phosphine−nickel(II) complex with methylated disilanes as the attacking species. These investigators also obtained considerable amounts of the hydrosilation product—formed by simple addition of an Si−H bond across an unsaturated bond—leading them to conclude that hydrosilation competes with the double silylation process.

To calculate the activation energy barrier for the addition of disilane to the π bond of ethylene, the double silylation reaction path is studied in the present work using various levels of theory. The gas-phase reaction is treated here in the absence of a catalyst, to establish baseline energetics against which future calculations that include catalysts may be compared. Ab initio studies of this reaction have not been undertaken in the past. However, the structures of the reactants and product in double silylation have been studied. Boatz and Gordon[11] calculated enthalpies of formation for the entire series of methyl-substituted disilanes at the MP2/6-31G(d) level of theory, while Profeta and co-workers[12] found optimized geometries for the trans and gauche conformations of 1,2-bis(silyl)ethane using the 3-21G* basis set and compared the molecule's rotational potential function with that of butane. More recently, Gordon and Day[13] studied the uncatalyzed hydrosilation reaction of ethylene with halogen-substituted silanes at the MP2/6-311G(d,p) level, finding the energy barrier of more than 50 kcal/mol to be insensitive to substituent effects. Since a Si−Si bond is weaker than a H−Si bond, one might expect a lower barrier for bis-silylation.

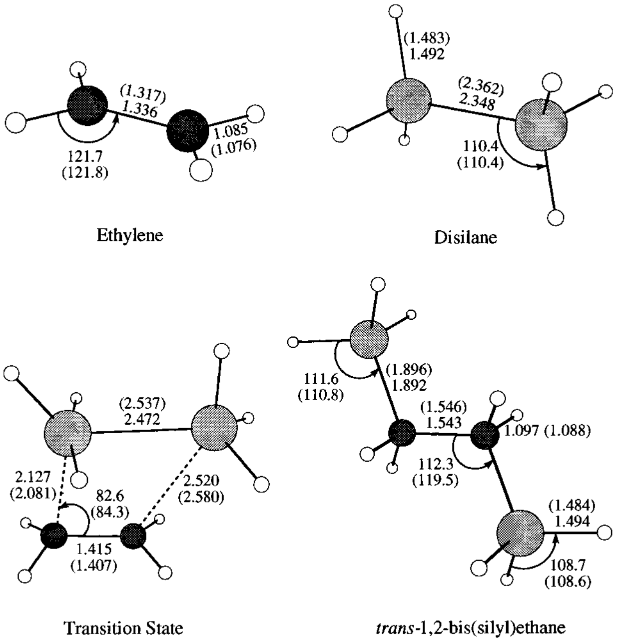

Figure 1. MP2/6-31G(d) optimized structures of stationary points on the double silylation potential energy surface, with RHF/6-31G(d) bond lengths and bond angles in parentheses. Bond lengths are in angstroms; bond angles are in degrees.

II. Computational Approach

Preliminary geometries and energies for the reactants and products (minima) and the transition states on the reaction path were obtained using the 6-31G(d) basis set[14] at the restricted Hartree−Fock (RHF) level of theory. The structures were then re-optimized with the 6-31G(d) basis set at the second-order Møller−Plesset perturbation (MP2) level of theory[15] to correct for electron correlation effects. The Hessians (matrices of energy second derivatives) were calculated by analytical means for RHF wave functions and by use of finite differences of analytic gradients for MP2. These Hessians were calculated and

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TABLE 1: Total Energies (hartrees) for Various Stationary Points Involved in the Addition of Disilane to Ethylene Using MP2/6-31G(d) Optimized Geometries

molecule	point group	MP2/6-31G(d)	MP4/6-311G(d,p)
CH_2CH_2	D_{2h}	−78.285 03	−78.382 42
SiH_3SiH_3	D_{3d}	−581.467 24	−581.626 30
transition state	C_s	−659.671 11	−659.928 86
$SiH_3CH_2CH_2SiH_3$	C_{2h}	−659.800 45	−660.056 31

TABLE 2: Relative Energies (kcal/mol) for the Gas-Phase Reaction of Ethylene and Disilane

	barrier height	exothermicity
RHF/6-31G(d) geometries		
RHF/6-31G(d)	73.9	24.4
RHF/6-311G(d,p)	75.3	23.1
MP2/6-31G(d)	51.4	30.5
MP2/6-311G(d,p)	48.3	33.2
MP2/6-31G(d) geometries		
MP2/6-31G(d)	50.9	30.2
MP2/6-311G(d,p)	47.9	33.1
MP4/6-311G(d,p)	50.1	29.9

diagonalized to obtain the harmonic normal modes and corresponding vibrational frequencies at both the minimum energy and transition-state geometries. Saddle points on the potential energy surface were indicated by one negative eigenvalue (i.e., one imaginary frequency), while local minima were characterized by a positive definite Hessian.

Once the identity of the stationary points as minima or saddle points was confirmed, the minimum energy path (MEP, steepest descent path in mass-weighted Cartesian coordinates) was followed from each transition state toward both reactants and products. The MEP verifies the identity of minima connected by a particular transition state, and it is frequently a useful starting point for the study of the reaction dynamics. Since the Gonzalez−Schlegel second-order integration method[16] was selected, a relatively large step size of 0.30 amu$^{1/2}$·bohr could successfully be utilized in locating consecutive points on the reaction path. Finally, single-point energies were calculated using fourth-order perturbation theory [MP4(SDTQ)][17] and the 6-311G(d,p) basis set[18] at the MP2/6-31G(d) geometries. All calculations were carried out by the electronic structure program GAMESS,[19] with the exception that the MP4(SDTQ) energies were performed by the Gaussian 92 program.[20]

III. Results and Discussion

The geometries of all stationary points involved in the double silylation reaction are illustrated in Figure 1. The total energies for these structures, as well as the relative energies of the reaction, are summarized in Tables 1 and 2, respectively. Comparison of the structures obtained with and without second-order perturbation theory reveals very little change.

Since the pathway with C_{2v} symmetry for the double silylation reaction is symmetry forbidden based upon the orbital symmetry rules of Woodward and Hoffman,[21] transition-state searches were carried out using starting geometries of reduced symmetry (C_s or C_1). It was initially expected that the transition state would feature a distorted approach of the disilane molecule toward the C−C double bond, so as to avoid the electrons in ethylene's π cloud. Transition states located previously for the hydrogenation of ethylene[22] and of disilene[23] demonstrate this tendency. The confirmed transition-state structure, however, shows the reactant molecules positioned such that the C−C and Si−Si bonds are virtually parallel, although the two forming Si−C bonds are quite different. It is an "early" transition state, resembling the reactants more closely than it does the products. This is consistent with the Hammond Postulate, in view of the predicted reaction exothermicity (see Table 2). The motion associated with the imaginary mode involves simultaneous C−C and Si−Si bond stretching, accompanied by eventual formation of the new Si−C bonds.

Table 2 contains energetic information for the bis-silylation reaction calculated from structures obtained at the RHF/6-31G-(d) and MP2/6-31G(d) levels of theory. As demonstrated in Table 2, the introduction of correlation results in a dramatic change in the energetics of the reaction. When a larger basis set and many-body perturbation theory are employed, the activation energy is reduced by over 25 kcal/mol and the exothermicity of the reaction is increased by nearly 9 kcal/mol. This is mainly due to the effect of correlation; the energetic changes due to basis set improvement alone are much smaller

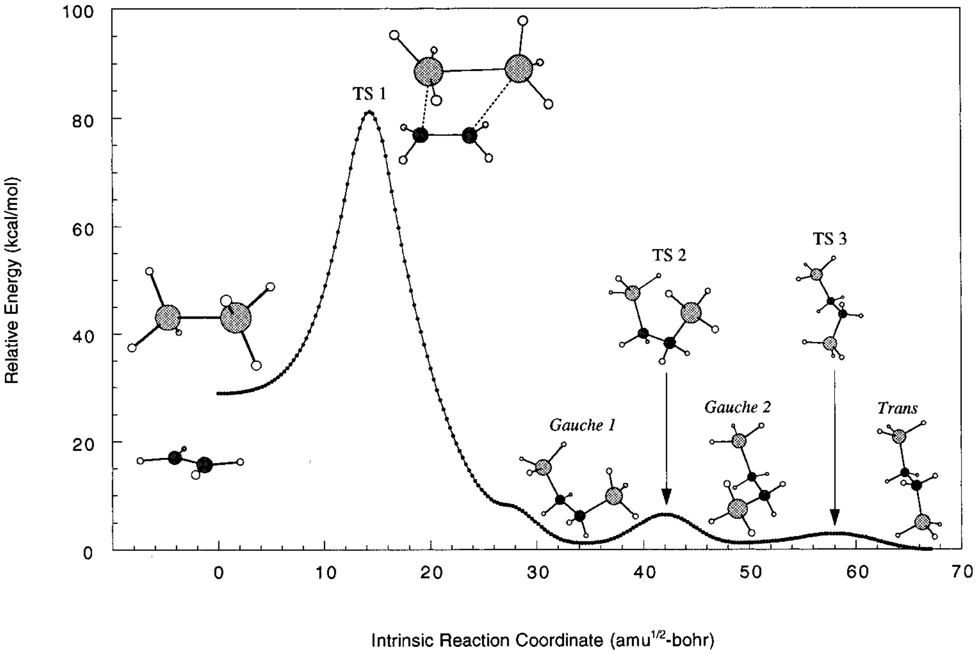

Figure 2. MP2/6-31G(d) minimum energy reaction path.

(approximately 3 kcal/mol). The MP2 energetics at the MP2 geometries are essentially the same as those obtained at the RHF geometries. MP4 single-point-energy calculations at the MP2 optimized geometries, using the larger 6-311G(d,p) basis set, resulted in very little change in the relative energies.

Figure 2 shows the MEP for the double silylation reaction, traced at the MP2/6-31G(d) level of theory (imaginary frequency $= 574i\ \mathrm{cm}^{-1}$). The RHF reaction path is very similar. The separated reactants, via an early transition state with C_s symmetry (labeled TS 1 in the figure), arrive at the second minimum on the potential energy surface: the gauche conformation of 1,2-bis(silyl)ethane, labeled Gauche 1. Although TS 1 has C_s symmetry, it is clear that the final product must rotate about the C−C bond. Therefore, the MEP calculation was performed in C_1 symmetry, and Gauche 1 indeed has C_1 symmetry. Spliced to this MEP is a second minimum energy path which leads from Gauche 1 to another gauche minimum (Gauche 2) via an internal rotational transition state of C_{2v} symmetry (TS 2). The MP2 rotational barrier at TS 2 is 4.9 kcal/mol. Finally, the trans version of the double silylation product, which is more stable than the gauche by 1.5 kcal/mol, is obtained by proceeding through a third transition state (TS 3) with a barrier of 1.3 kcal/mol. The barrier heights involved in these conformational changes, however, are quite small when compared with the barrier for the overall reaction.

It is worth noting that the actual reaction path contains a bifurcation point—a valley-ridge inflection—as it approaches the first gauche minimum (Gauche 1). That is, as the curvature of the potential energy surface in the vicinity of the minimum energy path changes from upward to downward (i.e., from valley to ridge), the actual reaction path splits into two symmetry equivalent channels that lead to two equivalent gauche minima. Since the C_s plane of symmetry is lost as one proceeds from the transition state toward the two gauche products, a bifurcation point must occur somewhere along this portion of the MEP. These two mirror-image products (Gauche 1 and Gauche 2) are transformed into each other via a transition state of C_s or higher symmetry (TS 2). The bifurcating channels converge to rejoin the MEP of Figure 2 at the most stable conformational isomer of the double silylation product, *trans*-1,2-bis(silyl)ethane. Of course, the minimum energy paths are static pathways, not dynamic trajectories. One would have to carry out trajectories in the vicinity of the MEP's to understand how the various minima on the potential energy surface are sampled.

IV. Conclusions

The addition of disilane across the π bond of ethylene is highly exothermic in nature but requires an activation energy of 73.9 kcal/mol at the RHF level using the 6-31G(d) basis set. Although this barrier falls to 50.1 kcal/mol once correlation is introduced, it remains large enough to indicate that the reaction will not occur easily in the gas phase. This is due primarily to the tremendous amount of initial translational kinetic energy that the reactant molecules must possess to cleave the stable Si−Si single bond homolytically. As suggested by experimental studies of double silylation, a transition metal catalyst [e.g., $\mathrm{Pt(PR_3)_4}$] is required for the reaction to proceed. Such a catalyst would provide an alternative, multistep mechanism for double silylation that involves a series of smaller energetic barriers to surmount. Due to the computational expense of including experimental catalysts in the calculations, one might employ the approach used by Musaev and Morokuma,[24] in which bulky ligands (R) have been replaced (e.g., PH_3 for PPh_3). Furthermore, molecular orbital (MO) methods can be combined with empirical molecular mechanics (MM), such that the catalyst's active sites are treated with MO and the rest with MM methods. These adjustments will make the calculations on such model catalytic systems only qualitatively comparable to experiment, but the results are nevertheless invaluable in the design and improvement of catalysts. The use of parallel electronic structure codes[19] will also render the inclusion of catalysts more feasible.

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