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Transition-state geometry and activation energy calculation for the retro-ene elimination reaction of propene from diallyl sulfide†

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ABSTRACT: The transition-state geometry and the activation energy for the retro-ene elimination of propene from diallyl sulfide were calculated at three levels of *ab initio* molecular orbital theory [HF, DFT(B3LYP) and MP2] combined with three basis sets (3–21G*, 6–31G* and 6–31 + G**). The activation energies were determined at room temperature and at 375 °C and compared with experimental data. Our calculations lead to transition states that consist of a non-planar six-center cyclic structure with a distorted chair-like geometry. Moreover, the transition-state geometry has a marked 'product-like' character. We found that the B3LYP/6–31G* level produce activation values closer to the experimental values in a reasonable time. In all cases studied, the activation energies obtained from both the density functional and MP2 are better than those obtained using the Hartree–Fock method, which overestimates the barrier height. Regardless of the level of theory used [HF, DFT(B3LYP) or MP2], the basis sets 6–31G* and 6–31 + G** produce practically the same values of the activation energy; however, the first set is about twice as fast as the second. The transition-state geometry obtained by different levels showed only slight structural differences.

KEYWORDS: *ab initio*; transition-state structure; retro-ene reaction; diallyl sulfide

INTRODUCTION

Over the past 10 years, it has become customary to calculate transition-state geometries for organic reactions that occur in a single step, even with modest computation recurrences. For instance, with a desktop computer is possible to obtain transition-state geometries with semiempirical methods for any reaction with a few atoms (up to ~20). The performance of the same calculation with *ab initio* methods substantially increases the computational time, and also hardware requirements.[1]

The geometry of transition states on the pathway between reactants and products is very difficult to detect and requires femtochemistry techniques,[2] and has been done only for the most elementary reactions. Despite the amazing advances in the experimental studies of transition states of simple chemical reactions, the only way to obtain detailed information on the geometries of the transition states of complex processes is to use quantum mechanical calculations. On the other hand, the values of activation energies are known for many organic reactions.[3] Regardless of the level of theory employed, generally the transition-state geometries obtained are similar and it is unnecessary to use a refined method with high computational requirements. However, in order to reproduce the experimental values of the activation energy, it is necessary to employ *ab initio* methods and a good basis set.[4] The most demanding computational problem is the correct evaluation of activation barriers for chemical reaction. Therefore, we prefer to focus on the calculation of activation energy rather than determining the precise geometry of the transition state.

The calculation of transition-state geometry and activation energy for pericyclic reactions is of special interest owing to the nature of the transition state. Pericyclic reactions have a cyclic transition-state structure in which all bond-forming and bond-breaking take place in concert, without the formation of an intermediate.[5] Among these, retro-ene reactions present an interesting situation owing to their complexity. The ene reaction, as originally defined by Alder *et al.*,[6] involves the addition of an olefin possessing an allylic hydrogen

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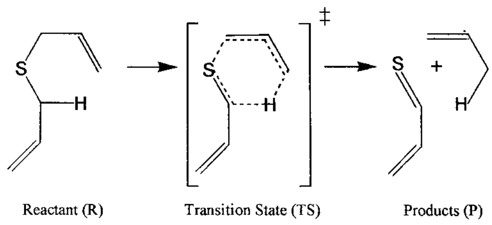

Figure 1. Retro-ene reaction of diallyl sulfide

(ene) to a compound having an electron-deficient multiple bond (enophile). On the other hand, the retro-ene reaction is related to both cycloadditions and sigmatropic hydrogen shifts, where one π bond is converted into a σ bond and, at the same time, a hydrogen atom is transferred in the process.[7] When bonds are formed to exactly the same extent in the transition structure, the reaction is called synchronous concerted; otherwise it is termed an asynchronous reaction.[8] Asymmetry in the starting materials introduces a level of asymmetry in the transition-state structure. Most pericyclic reactions are therefore concerted but asynchronous, since most pericyclic reactions do not have symmetrical components.[5]

Previous studies on the pyrolysis of diversely substituted allyl sulfides have permitted kinetic and mechanistic data to be obtained for this reaction.[9] A special case is represented by the pyrolysis of diallyl sulfide that occurs in the gas phase through a six-centered cyclic transition-state geometry as shown in Fig. 1.

As a continuation of our studies on the transition-state structures of propene elimination from allyl heteroelement systems,[10–12] we chose the retro-ene reaction of diallyl sulfide to verify previous results obtained for allyl methyl sulfide,[13] which were probed to explore the usefulness of different combinations between the various levels of theory and basis sets for computing activation energies. Moreover, size of diallyl sulfide is not large enough to allow transition-state structures to be obtained with a level as high as MP2/6–31 + G**.

Nowadays, chemistry teaching at undergraduate and graduate levels benefits enormously from computer advances. The computational searching and identification of the geometry of the transition states has become a very popular tool for studying chemical reactions. For instance, the retro-ene reactions as examples of pericyclic reactions have been a central focus of many calculations.[14] However, although there is a consensus on how to calculate barriers, it is not always possible to compute them at the most reliable level.[4]

For studying the transition states of ene reactions, the size of the molecules considered is crucial when selecting a computational method. The semiempirical methods, in particular AM1 and PM3, are perhaps the most widely used owing to their capacity to handle a large number of atoms.[10–12,15] The conventional *ab initio* method (Hartree–Fock) using moderate standard basis sets has been extensively applied to the study of these reactions[16–18] and MP2, CASSCF and DFT calculations have also been employed.[19–21]

The efficiency of the density functional theory (DFT) for calculate transition-state (TS) geometries in pericyclic reactions is a topic of great controversy. Some workers consider that DFT is not good for these kinds of calculation and they tend to underestimate the barrier heights,[22,23] whereas others suggest the contrary.[24–26] Further, in many cases, different calculation methods lead to different conclusions, e.g. Cramer and Barrows reported for [4 + 3] cationic cycloadditions a concerted TS structure employing HF and MP2, but DFT does not give this result.[27]

The majority of the theoretical work dedicated to transition-state structure searching in pericyclic reactions employs two or more methods.[13–15,17–26] For instance, Várnai and Kesarü[15] performed theoretical investigations on the retro-ene reaction of five different propargyl ethers using various methods and basis sets. They concluded that MP2 predicts an accurate barrier height for this kind of reaction.

Our goal here was to determine which combination between theoretical methods and basis sets is the most precise and fast for calculating accurate activation energies. With this in mind, we report activation energies computed from the combination of three levels of theory: Hartree–Fock (HF), second-order Møllet–Plesset (MP2)[28] and the density functional B3LYP scheme,[29,30] and three popular basis sets, 3–21G*, 6–31G* and 6–31 + G**.[31]

COMPUTATIONAL METHODS

All calculations were performed with the Gaussian 94 computational package.[32] The calculations were carried out on an SP2-IBM parallel computer at the National Scientific Center of the Andes University (CeCalc.ULA). The Chem3D program for PC was used for drawing and visualizing all the optimized structures.[33] Initial geometries for reactants and products were fully optimized. With this information, the program is capable of obtaining an intermediate from these two structures as a common middle point, i.e. the transition-state structure. For this calculation, the keyword SADDLE must be used, and the keyword FORCE produces the vibrational frequencies. It is broadly accepted that the hessian matrix with only one imaginary frequency is the best criterion for proving the transition-state structure.[34–38] The activation energy in this study was calculated as the energy difference of the sum of the total energy, plus zero-point energy (calculated at the corresponding level) and the thermal energy at 375 °C, between the reactant and the transition-state structure (hence we can to make a comparison with experimental data[9]).

Table 1. Activation energies for the retro-ene reaction of diallyl sulfide at 648 K (experimental activation energy = 138.2 kJ mol^{-1})

Method	E_a (648 K) (kJ mol^{-1})	E_a(calc.) − E_a(exp.) (kJ mol^{-1})	Time (min)
HF/3–21G*	222.8	84.6	38
HF/6–31G*	254.8	116.6	224
HF/6–31 + G**	254.5	116.3	543
B3LYP/3–21G*	120.4	−17.8	542
B3LYP/6–31G*	138.4	0.2	957
B3LYP/6–31 + G**	137.9	−0.3	1638
MP2/3–21G*	128.6	−9.6	167
MP2/6–31G*	136.6	−1.6	568
MP2/6–31 + G**	136.2	−2.0	953

RESULTS AND DISCUSSION

The nine calculated activation energies obtained at different levels are given in Table 1 for 648 K. The second column of this table shows the differences between the calculated and experimental activation energy values and the last column contains the total time for computing the transition states. This time includes the optimization time for reactants, products and transition states (searching and verifying). From this table we can make the following observations.

1. The HF method produces the highest calculated E_as. These values are much higher than the experimental values, whereas those calculated from MP2 and DFT are closer to the experimental values. It is logical that the density functional scheme and correlated method MP2 produce better results than the single HF hamiltonian.[28] These results are in concordance with those reported by Sosa *et al.*,[24] where the largest barrier height was obtained using the HF level.
2. The E_as obtained from the MP2 scheme are similar to those obtained with the DFT method. However, with basis sets of moderate size, 6–31G* and 6–31 + G**, the results are better with the DFT method. In particular, the small basis set 3–21G* produces closer results to experimental the values with the MP2 method.
3. Of the three methods tested the 3–21G* basis set always produces the lowest E_as, and again, the results from 6–31G* and 6–31 + G** are similar. This is a consequence of the analogy of the two last basis sets, despite the differences in computational time required, i.e. the costs of the calculations are different. For this reason, it is better to use the quick and economical basis set 6–31G* instead of the slow and expensive basis set 6–31 + G**.[4,13,15,36] Moreover, the similarity between the results from 6–31G* and 6–31 + G** is not surprising, as there are neither charged species nor congested lone pairs in our calculations.
4. The best calculated E_a was obtained from the combination B3LYP/6–31G*, but the E_a calculated with the combination B3LYP/6–31 + G** is almost as good. The use of the expensive basis set 6–31 + G** is unnecessary for this type of calculation.[13]
5. As indicated in the last column of Table 1, whatever the method utilized, the basis set 6–31 + G** requires the longest computing time, and hence it is impractical. Also, the method requiring that longest computational time was B3LYP; however, some authors suggest that DFT is an attractive methodology owing to the low computational cost.[25]

Large differences in activation energies between HF and post-HF methods show that the inclusion of correlation is essential in describing these barrier heights quantitatively. This situation corresponds to the first three cases (see Table 1). However, for the post-HF method the matching of theoretical and experimental values is remarkable with a basis set of moderate size.[26]

The geometries of the transition states obtained with different levels of theory are essentially the same. However, in the geometries of reactants and products some differences can be observed. In Fig. 2 are depicted the geometry of reactants, products and TS obtained with B3LYP/6–31G* (atomic numeration is included only for

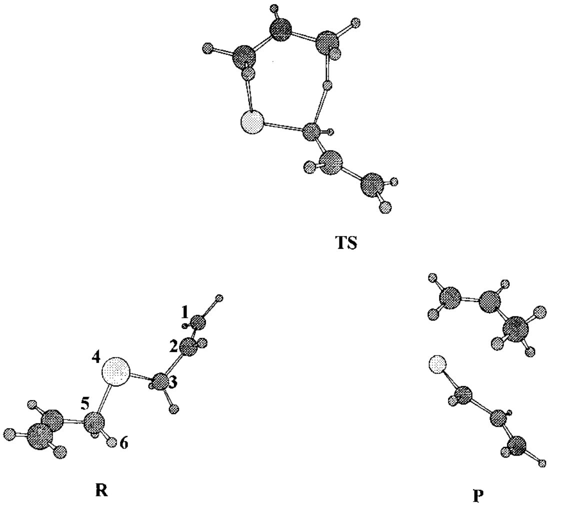

Figure 2. Reactant, transition-state structure and products for retro-ene reaction of diallyl sulfide

Table 2. Selected bond distances and bond angles for the R, TS and P obtained from the HF, B3LYP and MP2 methods with the 6–31G* basis set

Bond	R	TS	P
Bond distance (Å)—			
C1—C2	1.318/1.334/1.339	1.400/1.414/1.428	1.488/1.501/1.498
C2—C3	1.482/1.499/1.496	1.376/1.398/1.411	1.317/1.334/1.339
C3—S4	1.824/1.851/1.826	2.344/2.267/2.295	5.000/5.000/5.000
S4—C5	1.824/1.851/1.826	1.690/1.717/1.709	1.607/1.637/1.630
C5—H6	1.085/1.095/1.095	1.422/1.464/1.510	4.784/4.856/4.803
H6—C1	5.328/5.567/5.456	1.309/1.312/1.355	1.086/1.097/1.094
Bond angles (°)—			
C1—C2—C3	124.4/124.3/123.7	119.1/118.9/117.2	124.9/124.5/123.9
C2—C3—S4	110.0/109.7/109.3	99.5/99.8/100.4	90.0/90.0/90.0
C3—S4—C5	99.9/99.6/98.9	101.1/101.4/101.9	90.0/90.0/90.0
S4—C5—H6	108.2/109.6/110.1	100.9/100.4/99.7	107.2/108.8/108.0
C5—H6—C1	62.1/65.7/64.3	157.9/159.8/158.8	103.1/103.4/104.5
H6—C1—C2	21.5/24.4/26.2	99.7/99.4/101.1	111.2/111.2/111.2

the reactant). The geometry plots for the studied reaction obtained from other levels of theory are almost indistinguishable. Table 2 gives the bond distances and angles of the selected bonds for reactant (R), transition state (TS) and product (P) obtained with the HF, B3LYP and MP2 methods with the 6–31G* basis set. The atomic numeration used in Table 2 is the same as in Fig. 2.

Table 2 shows that all methods used lead to similar transition-state geometries. In the geometries of transition states (TS column in Table 2) the bond distances calculated by different levels of theory vary very little, always by less than 0.08 Å. For the bond angles the difference is always less than 2°. This means that the use of any level of theory produces a consistent geometry of the transition states.

Some remarks must be made concerning Table 2. The variations in bond distances and bond angles clearly show how the reaction occurs. For example, the variation in the C1—C2 distance shows how it is transformed from a double to a single bond, whereas an inverse change occurs for the C2—C3 bond. An important detail concerns the relative array positions between the products of reaction. To keep the propene and the thiopropenal molecules well separated in the products, the C3—S4 distance and the C2—C3—S4 and C3—S4—C5 angles are fixed during the optimization of the products. This is a necessary condition for the use of the keyword SADDLE in the Gaussian program.[1]

The H6—C1 distance, where the transferable hydrogen (H6) is involved, indicates the movement of this atom from C5 in the reactant to C1 in the product. A particular change is observed for the S4—C5—H6 angle, because the angle in TS needs to be lower than its value in R and P. The same change occurs for the C1—C2—C3 and C2—C3—S4 angles; the value in TS is lowers than those in R and P. In general, the values for the distances obtained with the HF method tend to be shorter than those obtained using other methods.[23]

Table 2 also contains some meaningless data that correspond to unconnected atoms for the reactant and product, but they are very important in the transition-state structure, e.g. instance, the H6—C1 distance in the reactant and the C5—H6 distance in the product. The same occurs for the C5—H6—C1 and H6—C1—C2 angles in the reactant and all angles in the product, except C1—C2—C3 and H6—C1—C2. Obviously, this is a consequence of the rupture of the C3—S4 bond in the reaction.

From both Fig. 2 and Table 2 it is easy to see that the transition-state geometry has a clear 'product-like' character. The values of the distances and angles in the TS are closer to the respective values in the products. This is contrary to the results obtained for cyanomethyldiallylamine, where the TS geometry has a marked 'reactant-like' character.[12]

CONCLUSIONS

We have shown how the use of the right combination of method and basis sets can give excellent values for activation barriers. Usually, to obtain the best activation barrier it is necessary to employ a high level of *ab initio* calculation with large basis sets, but this is very expensive. On the other hand, the geometry of the TS computed by the most economical method–basis set combination is very similar to that obtained with the expensive combinations. It must be mentioned that the activation barriers computed with HF, in most cases, differ considerably from the experimental data. Therefore, we do not recommend these methods for evaluating reaction activation barriers. More reliable activation barriers can be obtained with a high-level *ab initio* method such as B3LYP and MP2 calculations. Excellent results were obtained here with the combination B3LYP/6–31G* for diallyl sulfide, in concordance with previous results.[13] Nevertheless, the HF method computes geometric parameters for the transition-state structure that are, in many cases, similar to those from high-level DFT or MP2 calculations.

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