

Chapter 14: Transition States

Key Notes:

Fundamental Aspects

Chemists have devised a number of theories to help explain and understand chemical reactions. *Collision theory* assumes that reactant molecules must collide with the proper orientation and with energy greater than some minimum value known as the activation energy (E_a). *Transition-state theory* states that two colliding molecules form an activated complex, or transition state, which is an unstable grouping of atoms. The activated complex can fall apart in different ways and revert to reactants or yield products. The *Arrhenius theory* describes the relation between the rate constant k , the temperature T , and E_a . The activation energy is the difference between the energy of the *transition structure* and the energy of the reactants. The transition structure and its energy can be calculated, as well as the energy of the reactants and products. Computational chemistry has become an important tool in advancing our knowledge of how reactions occur.

Potential Energy Surfaces

A plot of how the potential energy of a system changes as a function of structure is called a potential energy surface. Potential energy surfaces have several important features. The energy *minima*, or valleys, correspond to the equilibrium structures of a given molecule, or to the relative energy of a reactant and product. For the potential energy surface of a simple reaction $A \rightarrow B$, the path between the minima for A and for B is the *reaction path* or *profile*, sometimes called the *reaction coordinate*. The reaction coordinate will typically have a maximum in energy at a *saddle point*. The geometry found at the saddle point is the *transition structure*, and the energy of this structure can be used in finding the activation energy for a reaction.

Reaction Coordinate

The potential energy diagrams that plot energy vs. reaction coordinate (or “progress of reaction”) that chemists regularly employ are cross sections of the full potential energy surface that describes the system. These simplified diagrams are useful in visualizing activation energies and whether reactions are exothermic or endothermic. They are also commonly used to illustrate the decrease in activation energy in catalyzed chemical reactions.

Calculating Transition Structures

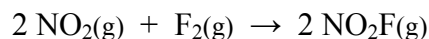
Finding the correct transition structure geometry can be difficult and involves trial and error. There are various methods that can be used, and chemical intuition is an important factor. Many computational software packages have “transition state optimization” routines that can be helpful. Once a possible structure is identified, an IR calculation (Chapter 13) should reveal one imaginary (negative) frequency. This frequency corresponds to atomic motions that lead towards lower energy structures. If one imaginary frequency is found for the candidate structure,

this means the structure is indeed at a saddle point, but it may *not* be the saddle point on the reaction path connecting reactants and products! If the correct transition structure has been found, animation of the normal vibrational mode that corresponds to the imaginary frequency should show that the atomic motions lead in the direction of reactants and products.

Fundamental Aspects

Chemists would like to know the details of how chemical reactions occur on an atomic level. Why do certain reactions take place, but not others? If a single molecule undergoes some type of rearrangement, how are the old bonds broken and the new bonds formed? If a given molecule has equivalent bonds, do they break simultaneously or one at a time? If a reaction gives a mixture of products, what factors are responsible for the product ratio? Why are some reactions fast while others are slow, and why do reaction rates depend on temperature? A number of theories have been devised over the years in order to provide answers to questions such as these. Experimentally, this is a difficult task given the small distances and very short timescales involved. Recent work in femtosecond (10^{-15} s) spectroscopy has begun to answer some of these questions, and computational results on transition structures continue to provide important insight.

The rate of a chemical reaction depends on the temperature. For the reaction:



The experimental rate law, which relates the rate of a reaction to the concentration of reactants, is given by:

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

The square brackets denote molar concentration. Experiments show that the rate constant (k) varies with temperature. In general, the reaction rate increases with increasing temperature. *Collision theory* explains the temperature dependence of rate constants by assuming that reactant molecules must collide with energy greater than some minimum value (the activation energy E_a) and that the collision orientation must be correct for a reaction to occur. As the temperature increases, the gas phase molecules in the above reaction will be moving faster resulting in more collisions. Increased molecular speed means increased kinetic energy, so more of the collisions will have energy greater than E_a . The orientation requirement is temperature independent. *Transition-state theory* goes further in postulating that colliding reactants form an activated complex (transition state) that can break up to either reform reactants or go on to form products. In thermodynamic terms, this theory relates the rate constant to the *Gibbs free energy of activation* (ΔG^\ddagger) which is equal to the difference in Gibbs free energy between the transition state and the reactants. The geometry of the *transition state* referred to here is at the peak of the Gibbs free energy (G) reaction profile, not the potential energy reaction profile. Note that the geometry of the *transition structure* discussed above occurs at the maximum of the potential energy reaction profile. While we typically refer to the “transition state”, what we often really mean is the “transition structure”.

From the computational standpoint, one approach is to use the Arrhenius theory which relates the rate constant (k) to the activation energy (E_a) via:

$$k = Ae^{-E_a/RT}$$

where A is the frequency factor
 e is the base of the natural logarithm
 R is the ideal gas constant
 T is the absolute temperature

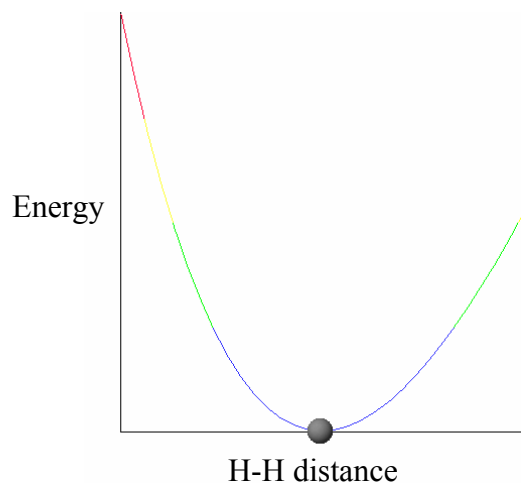
Experimentally, a plot of $\ln k$ vs. $1/T$ should give a straight line whose slope is $-E_a/R$ and intercept is $\ln A$. We can also *calculate* the energy of a transition structure and obtain E_a via:

$$E_a = E_{\text{transition structure}} - E_{\text{reactants}}$$

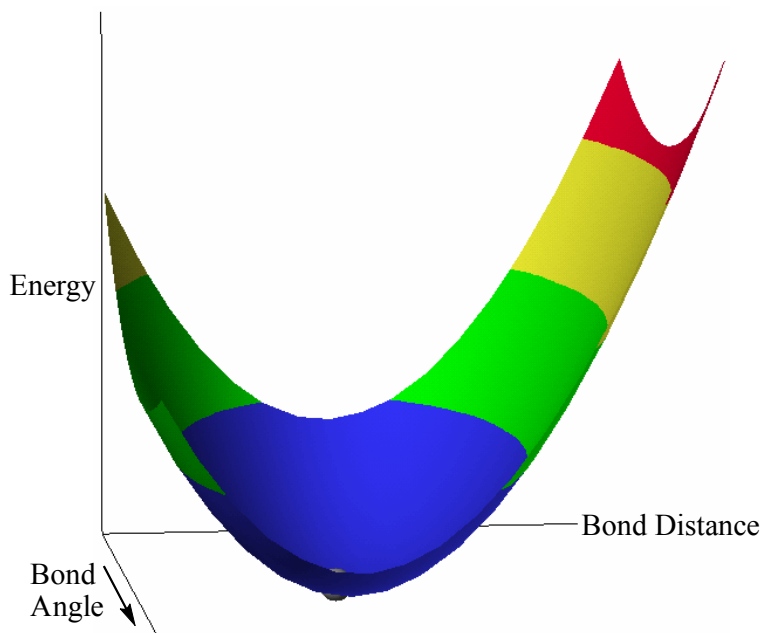
The Arrhenius theory is approximate and absolute values of the frequency factor A are hard to calculate. It is thus very difficult to calculate absolute rate constants with any degree of accuracy. If we can make A values cancel out (e.g. by looking at ratios of rate constants) we can obtain quite useful results.

Potential Energy Surfaces

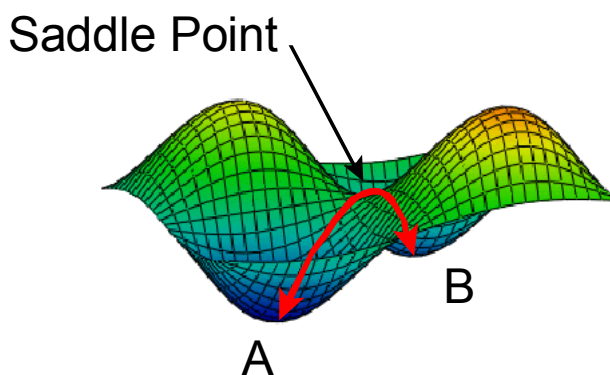
A potential energy surface shows how the energy depends on structure. The surface will have as many dimensions as the total number of degrees of internal motion of the system being studied. A diatomic molecule ($N = 2$) will have only one degree of internal motion, which is the bond length ($3N - 5 = 1$). The potential energy surface in this case is a simple two-dimensional plot of energy vs. bond distance, as shown below for the H_2 molecule.



For a symmetric nonlinear triatomic molecule like H_2O , a three-dimensional potential energy surface plots energy (z -axis) vs. O-H bond length (assuming both O-H bond lengths are identical) and H-O-H bond angle (x and y axes).



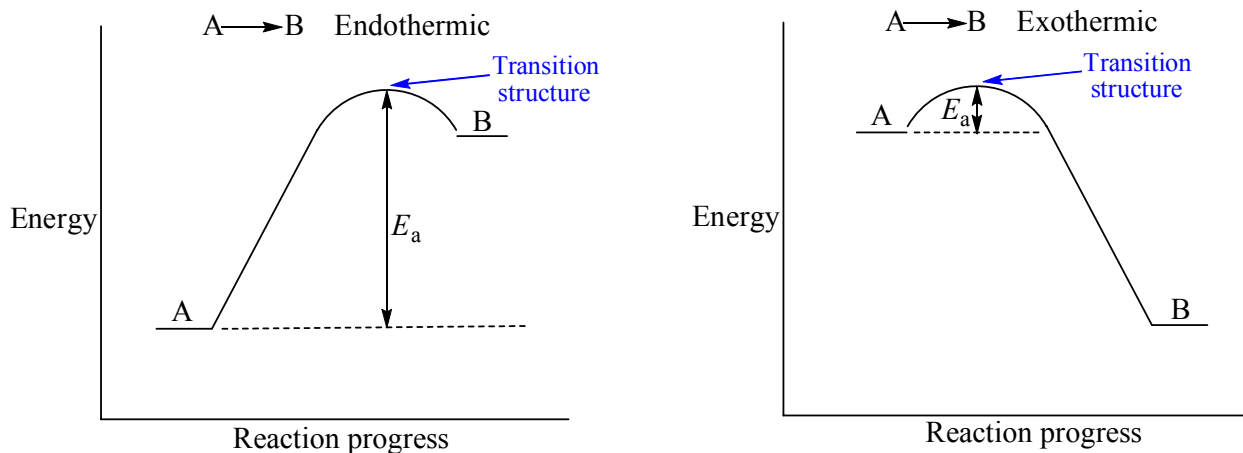
Systems involving more than two structural parameters cannot be plotted. For a simple reaction such as $A \rightarrow B$, a potential energy surface can show the relative energies of reactant and product, and the minimum energy path, or reaction coordinate (shown in red below) between them:



The highest energy structure along the reaction coordinate shown above is the transition structure, which lies on the saddle point. A saddle point lies at a maximum in energy along one direction (the reaction coordinate) and is at a minimum of energy in all directions other than the reaction coordinate (see above). If we correctly identify the transition structure, it should have one imaginary frequency whose normal mode reflects atomic motions that lead to reactants or products.

Reaction Coordinate

Chemists often simplify the figure above showing the potential energy change of the general reaction $A \rightarrow B$ by looking at a cross section of the diagram in two dimensions. From the above diagram, it appears that the reaction is endothermic (reactants have lower energy than products; reaction absorbs heat), as shown on the left:



A general exothermic reaction (reactants have higher energy than products; reaction releases heat) is shown on the right. These diagrams make clear that E_a is the difference in energy between the reactant(s) and the transition structure. An analogous physical situation involves rolling a heavy ball from one valley, over a hill, then letting it roll down into another valley. The amount of work done “rolling uphill” represents E_a . Our ability to computationally model a transition structure and calculate its energy (and the energy of reactants and products), is much easier than going through the experimental process described above. Comparison of experimental and calculated E_a values shows that, depending on the level of theory we use and the computational expense we are willing to deal with, that very good results can be obtained. Reactions involving dangerous substances and those that are otherwise difficult to follow experimentally can now be explored using computer technology.

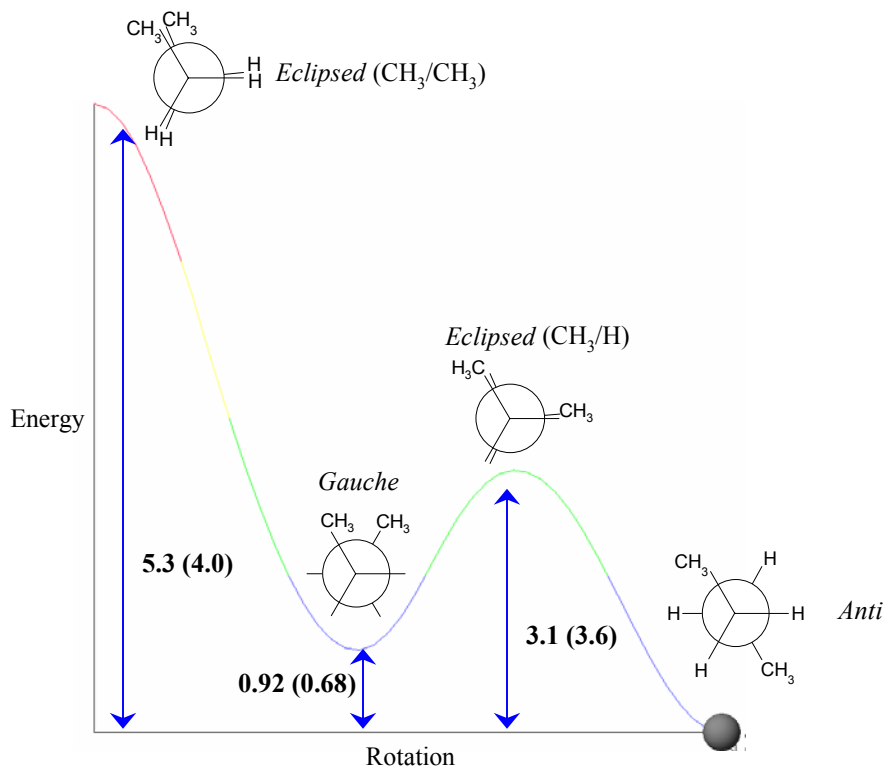
Calculating Transition Structures

As chemists work to further their understanding of chemical reactivity, the ability to compute transition structures has provided great insight. However, the calculations can be difficult, and the methods used all involve some trial and error. Chemical intuition can assist in providing a framework for an initial guess. The difficulty lies in finding the correct geometry for the transition structure. We can verify that our transition structure may be a good one by calculating the IR spectrum (Chapter 13). If the structure we have found is indeed at a saddle point on the potential energy surface, we should see one imaginary (negative) frequency value. However, it is possible we are at the *wrong* saddle point on the potential energy surface – *not* the one that connects reactants and products! Many programs used to calculate vibrational frequencies allow animation of the atomic motions for a given normal mode. If the transition structure we have found is indeed at the correct saddle point that connects reactants and products, animation of the imaginary frequency should reveal atomic motions that lead in the direction of reactants (bond breaking) and products (bond formation).

As discussed in Chapter 11, the geometry optimization process leads to what is called a

stationary point on the potential energy surface. A stationary point may be a minimum (local or global) on the potential energy surface, or a maximum (local or global). If we are at a minimum, all of the calculated vibrational frequencies will be positive values. A transition structure will lie at a saddle point (local maximum) and can be identified by one imaginary (negative) vibrational frequency. The trick is to build a geometry that is close enough to the transition state so that optimization will find the correct transition state geometry. Most software programs include a “transition state optimization” routine. Once a good guess at the transition state geometry is built, this routine can assist in finding the transition state, but this approach may not always work. Finding a good transition state will often involve some trial and error. Always perform an IR calculation and check for one imaginary frequency. Explore the animation of this frequency and see if the atomic motions lead towards reactants and products. Several examples of increasing complexity are provided below.

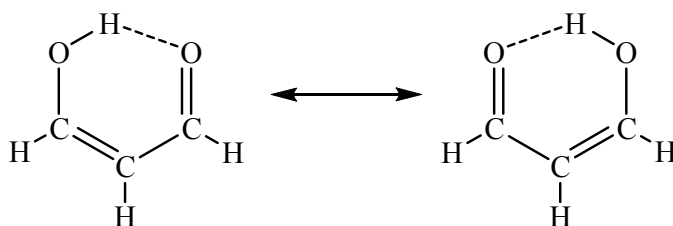
Example #1: Conformations of n-butane. As we rotate around the C₂-C₃ bond in butane, we form various conformers of different energy. The highest energy conformer (global maximum) occurs when the two methyl groups are eclipsed, due to the van der Waals (steric) repulsion between them. The minimum energy conformer (global minimum) occurs when the two methyl groups are pointing in opposite directions, or *anti*. Another maximum (local maximum) occurs when the methyl groups are eclipsed with hydrogen atoms. A local minimum is found in the *gauche* conformer, as shown below:



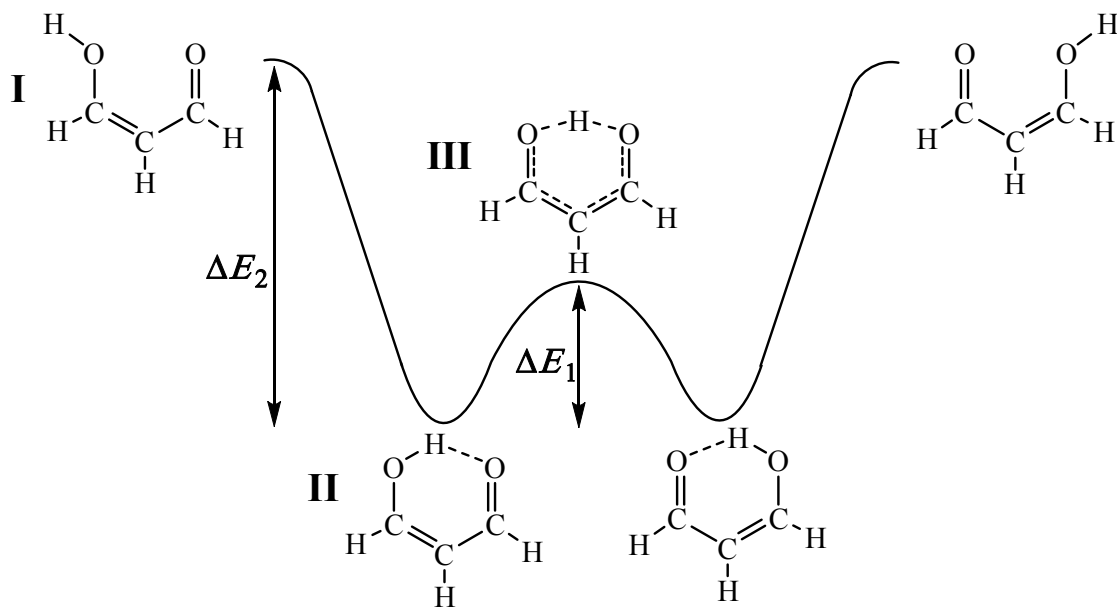
The numbers for the relative energies of the different conformers were calculated using DFT (B88-LYP, DZVP) and are in kcal mol⁻¹. Experimental values are in parentheses. Each of the four structures shown in the above figure was constructed, and a geometry optimization was performed in each case to obtain the energy. The C₁-C₂-C₃-C₄ angle was fixed at 120° for the

lower energy eclipsed conformation, at 60° for the *gauche*, and at 0° for the highest energy eclipsed conformation. To ensure that minima were located for the *anti* and *gauche* conformations, IR frequency calculations were performed on the optimized structures, and all frequencies found were positive. Similarly, IR frequency calculations performed on the two eclipsed structures each gave one imaginary (negative) frequency value, confirming that transition structures had indeed been found. Differences in energy values were calculated, and the experimental values were found on the National Institute of Standards and Technology's Computational Chemistry Comparison and Benchmark Database website (See: <http://srdata.nist.gov/cccbdb/exprotbar.asp>).

Example #2: Proton Transfer in Malonaldehyde Enol. This compound is the simplest system that has an *intramolecular* proton transfer between two oxygen atoms, as shown below:



It's pretty easy to guess what the transition state would look like. The proton would be equally shared between the two oxygen atoms. In the two structures shown above, we would also expect some hydrogen bonding between the oxygen-bound proton and the carbonyl (doubly bonded) oxygen. This is indicated with the dashed "weak bond" line. If the proton bound to the oxygen were turned away from the carbonyl oxygen, no intramolecular hydrogen bonding would be present, and we would expect such a molecule to be at higher energy. So, we have three structures whose energy needs to be calculated. Two of them will also have IR frequency calculations performed to make sure they are minima and maxima (saddle point) on the potential energy surface. The calculations were performed using density functional theory [B3LYP/6-31G(d)]. The results are shown below:

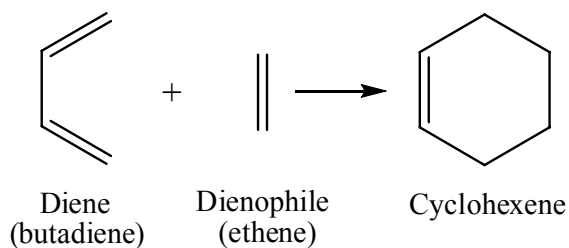


The difference in energy between compounds **II** and **III** in the above diagram (ΔE_1) is 3.5 kcal mol⁻¹ (lit. value 4.0). Compounds **I** and **II** differ in energy (ΔE_2) by 15.0 kcal mol⁻¹ (lit. value 12.4). To further understand the changes in structure which occur during the proton transfer, various bond lengths for compounds **I**, **II**, and **III** are collected in the following table. “Left and “right” bond lengths refer to the structures above.

Bond length (Å)	Cmpd. I	Cmpd. II	Cmpd. III
O-H (left)	0.969	1.005	1.215
O-H (right)	n/a	1.689	1.215
C-O (left)	1.346	1.322	1.282
C-O (right)	1.219	1.244	1.282
O- - - -O	2.865	2.590	2.378
C-C (left)	1.350	1.367	1.401
C-C (right)	1.465	1.439	1.400

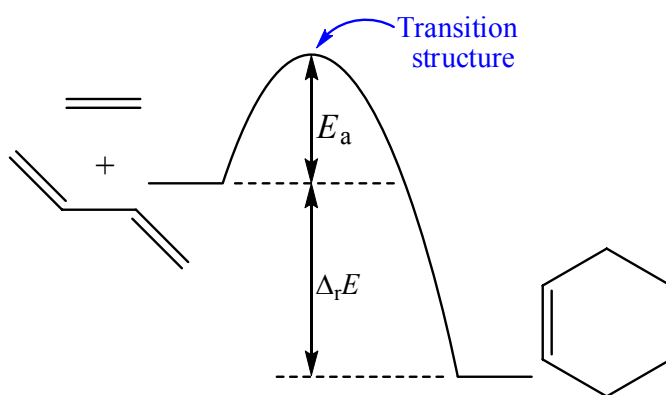
From the values in the first row of the table, the O-H bond length increases as the bonding to the second O atom increases. The C-O bond on the left shortens with increasing double bond character, while the C-O bond on the right lengthens. The two O atoms move substantially closer in the transition state as the proton becomes equally shared just before transfer. The C-C bond lengths also change during the process. It is these details of a reaction revealed by computation that greatly increases our understanding of chemical reactivity.

Example 3. Diels-Alder Addition of Butadiene and Ethylene. Our last example involves two separate reactant molecules that combine to form a single product. The Diels-Alder reaction is a synthetically useful example of such a system. In this reaction a conjugated diene reacts with an alkene (the dienophile) to form a 6-membered ring:

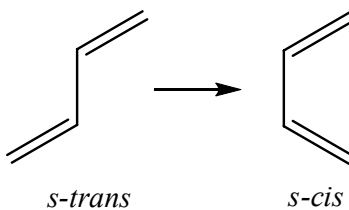


The diene has four π electrons while the dienophile has two π electrons. This reaction is thus known as a [4 + 2] cycloaddition. Four of the six π electrons present in the reactants are used to make the two new σ bonds in the product.

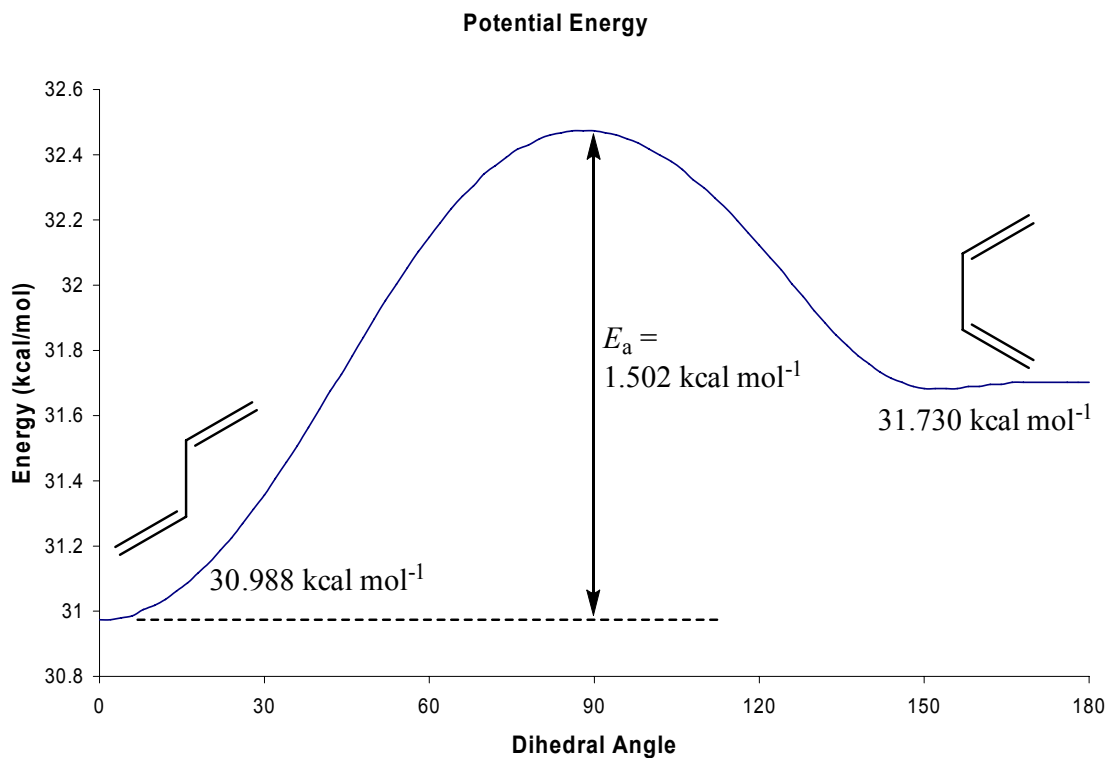
The reaction can be summarized in the following potential energy diagram:



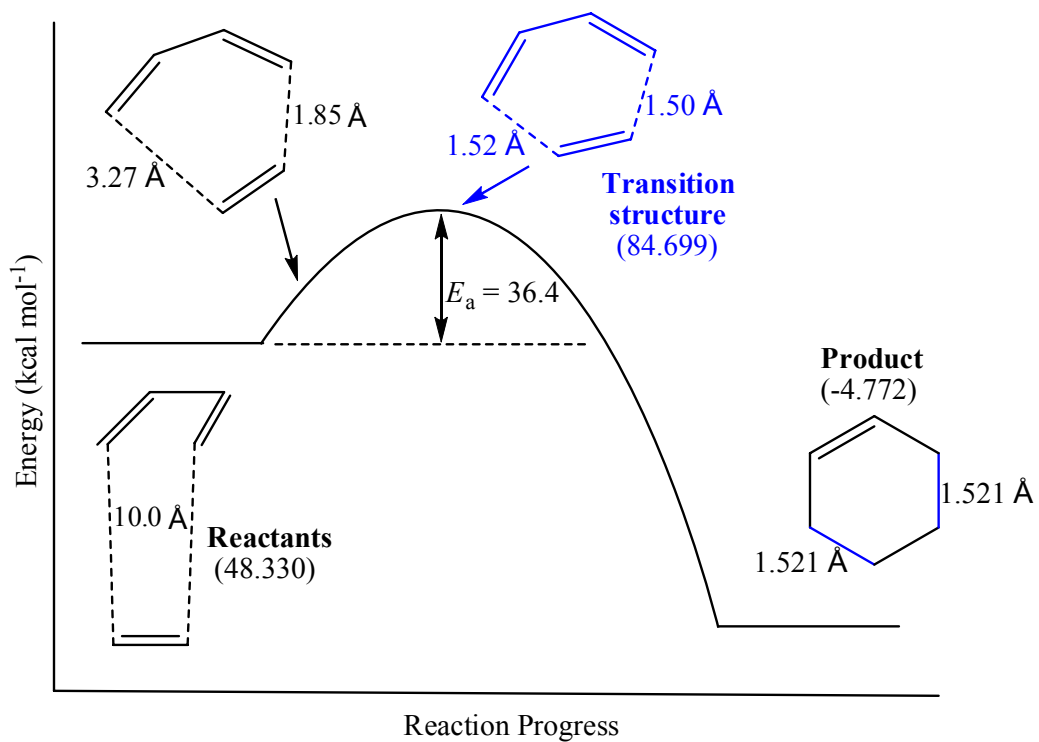
The most stable form of butadiene is the *s-trans* form. In order for the cycloaddition reaction to occur, butadiene must be in the higher energy *s-cis* form:



To find the energy difference between these two conformers, we follow a procedure similar to that from Example #1 above. The calculation was performed using the semiempirical PM3 method:



To find E_a for the cycloaddition reaction, the potential energy of the reactants is calculated when they are well-separated and also as they are brought closer and closer together. An energy maximum is reached (transition structure), and then the product is formed. The calculation was again performed using the PM3 method. Energy results for reactants, transition state, and product are given in parentheses. Carbon-carbon distances for the new bonds are also given:



The E_a value of 36.4 kcal mol⁻¹ does not compare very well with the literature value of 27 ± 2 kcal mol⁻¹, but accurate quantitative results are not to be expected using the PM3 method.