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Are Intermediate, Activated Complex, Transition State And Adduct The Same? And What Does The Reaction Coordinate Mean? A One Hour Class-Room Lecture For Graduate Students

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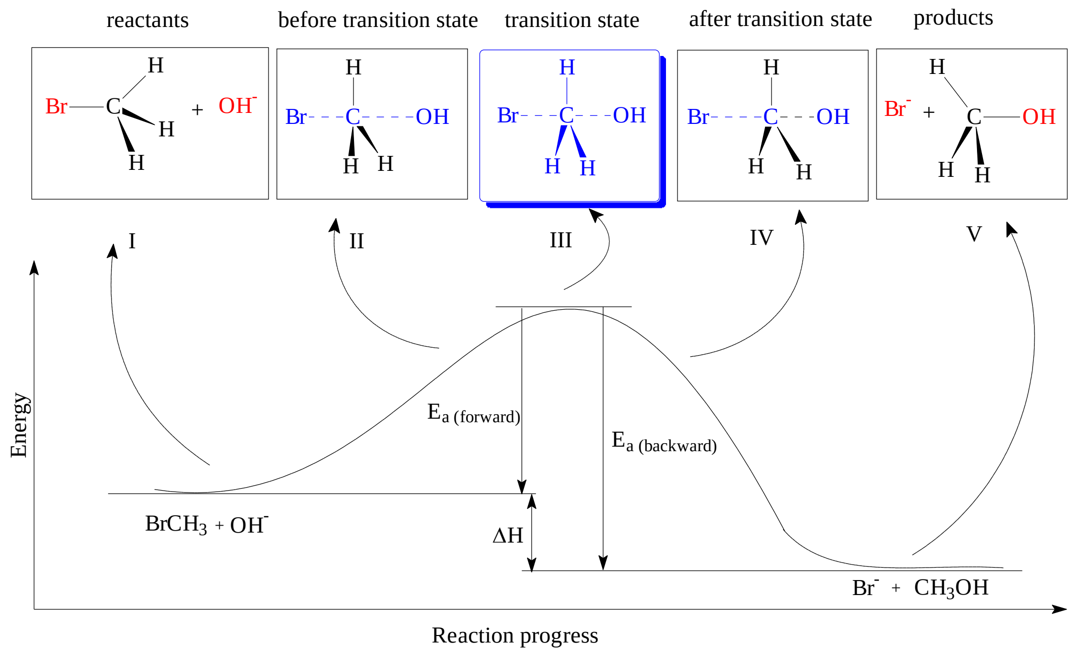
ABSTRACT

As a physical organic chemistry student and as a teacher nearly for the last three and half decades teaching to undergraduate and post-graduate students, it is often observed that still an excellent class room teaching is an art and a good teacher should note that the fundamentals should be taught comprehensively. As kineticists we can say that chemical kinetics continues to move ahead on many fronts, one of them in which kineticists are increasingly interested is the Physical Organic Chemistry. Though physical organic chemistry teachers often teach the description of the intermediate, activated complex, transition state and adduct in a class-room of organic reaction mechanism and chemical kinetics with differences in their meanings, still the average and above average students conceive them that they always convey the same meaning.

Keywords: Intermediate, activated complex, transition state, adduct.

DISCUSSION

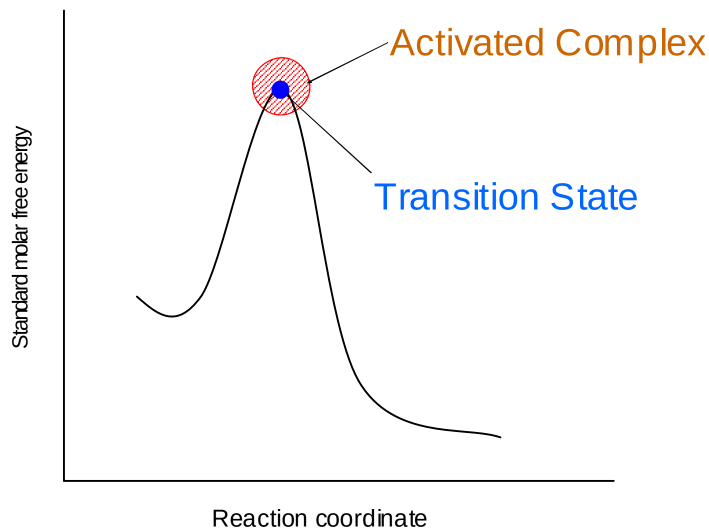
In the transition state theory, the mechanism of interaction of reactants is not considered; the important criterion is that colliding molecules must have sufficient energy to overcome a potential energy barrier (the activation energy) to react. For a bimolecular reaction, a transition state is formed when the two molecules' old bonds are weakened and new bonds begin to form or the old bonds break first to form the transition state and then the new bonds form after. The theory suggests that as reactant molecules approach each other closely they are momentarily in a less stable state than either the reactants or the products. In the example below, the first scenario occurs to form the transition state. It takes a lot of energy to achieve the transition state, so the state is a high-energy substance. The potential energy of the system increases at this point because: The approaching reactant molecules must overcome the mutual repulsive forces between the outer shell electrons of their constituent atoms.



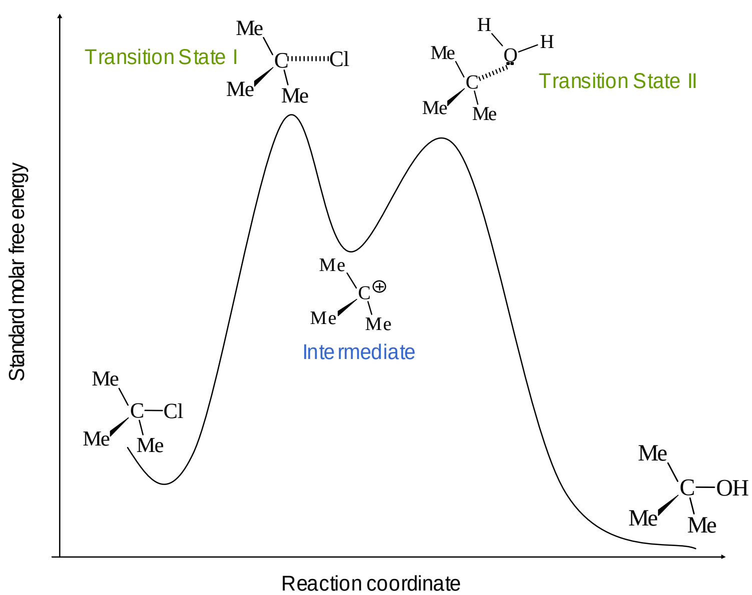
And the atoms must be separated from each other as bonds are broken. This increase in potential energy corresponds to an energy barrier over which the reactant molecules must pass if the reaction is to proceed. The transition state occurs at the maximum of this energy barrier. The transition state is an unstable transitory combination of reactant molecules that occurs at a potential energy maximum.

In order for a reaction to take place, molecules of the reactants must come in contact with each other. The collision theory of chemical kinetics states that the rate of a reaction is proportional to the frequency of the collisions between the molecules. Not only must the molecules come in contact with each other to react, but their energies must be great enough to overcome the repulsive force that molecules experience at extremely small separations. When the molecules collide, they form a transition state, during which the molecules form a large, loosely bound conglomerate. The conglomerate is called an activated complex. The activated complex is an unstable intermediate step where bonds break and form to generate the products or degenerate back to reactants. Since an activated complex is not stable, it requires a large amount of energy to force the molecules close enough together to attain this form. The required energy is known as the activation energy, as given by the Arrhenius equation. The collision theory provides the theoretical basis for the Arrhenius equation. Both of these can best be represented by the following potential energy diagram:

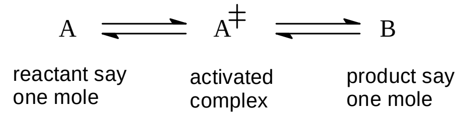
Activated Complex and Transition State



In conclusion an activated complex is the cluster of atoms or molecules that corresponds to the region close to the maximum energy. The transition state is the one which has a crucial configuration at energy maximum within the region of the activated complex and which has no lifetime, whereas an intermediate has finite lifetime. The following figure can best explain the meaning of activated complex and intermediate taking solvolysis of t-butyl chloride in water as a typical example.

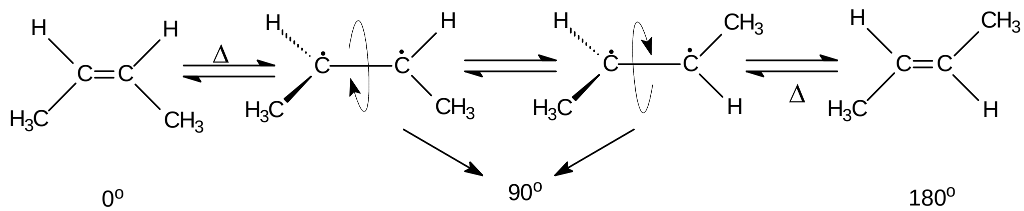


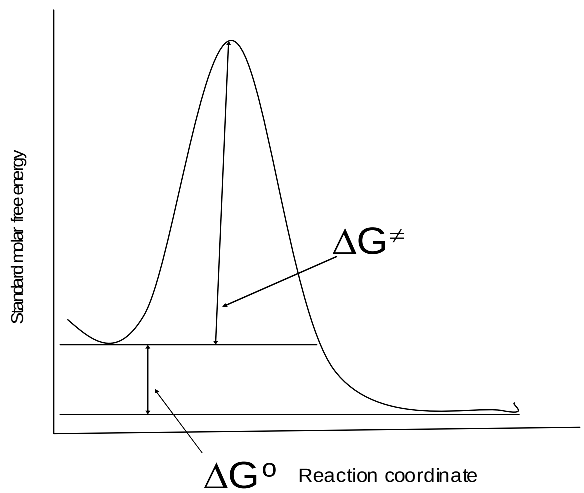
Now what does the reaction coordinate mean? Consider a reversible reaction



And this involves a change in free energy. If the initial and final states are standard states of A and B, then the change is the standard molar free energy of the **r**eaction i.e. $\Delta_r G^o$. However, the process is not instantaneous and we can consider initial and final states to be separated in the *reaction coordinate* by a standard free-energy maximum or barrier. Reaction coordinate is not a definite property but it is to be understood that it is the course of the independent individual reaction events. For example if it is bimolecular collision in a gas phase reaction, it may be a change in bond length in the reactants and products. Or it may be a change in bond angle in a molecule.

For example, consider a unimolecular thermal isomerization of one molecule of *cis*-2-butene in to *trans*-2-butene.





One can represent the reaction coordinate for this isomerization approximately as the dihedral angle between the two methyl groups which will change from 0° for *cis* to 90° for the activated complex to 180° for *trans* or in the reverse direction 180° to 0°. But some other properties also change in this reaction like the change in C_2-C_3 bond, C-H in C_2 and C_3. The change in torsional angle does not necessarily give the contribution toward the potential energy of the molecule but all other events should be put together.

However the change in dihedral angle is just enough to take for understanding the reaction coordinate.
Finally, an adduct is a new chemical species AB, each molecular entity of which is formed by direct combination of two separate molecular entities A and B in such a way that there is change in connectivity, but no loss, of atoms within the moieties A and B. Stoichiometries other than 1:1 are also possible, e.g. a

bis-adduct (2:1). An "intramolecular adduct" can be formed when A and B are groups contained within the same molecular entity .

And in biology, an adduct is a complex that forms when a chemical binds to a biological molecule, such as DNA or protein.

It could be a product formed by the addition of a diene with another unsaturated compound (as maleic anhydride). And a Lewis adduct is one which would be formed between a *Lewis acid* and a *Lewis base.* There are several other adducts like σ-adduct, π-adduct and Meisenheimer adduct.

REFERENCES

[1] Any *physical organic chemistry* text books available in the chemistry libraries.