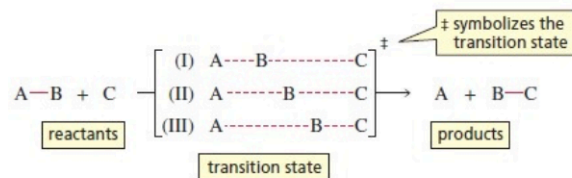


The Structure of the Transition State

Knowing something about the structure of a transition state is important when you are trying to predict the products of a reaction. In Section 3.7, you saw that the structure of the transition state lies between the structure of the reactants and the structure of the products. But what do we mean by “between”? Does the structure of the transition state lie exactly halfway between the structures of the reactants and products (as in II in the following diagram), or does it resemble the reactants more closely than it resembles the products (as in I), or is it more like the products than the reactants (as in III)?



According to the **Hammond postulate**, the transition state is more similar in structure to the species to which it is more similar in energy. In the case of an exergonic reaction, the transition state (I) is more similar in energy to the reactant than to the product (Figure 4.3, curve I). Therefore, the structure of the transition state will more closely resemble the structure of the reactant than that of the product. In an endergonic reaction (Figure 4.3, curve III), the transition state (III) is more similar in energy to the product, so the structure of the transition state will more closely resemble the structure of the product. Only when the reactant and the product have identical energies (Figure 4.3, curve II) would we expect the structure of the transition state (II) to be exactly halfway between the structures of the reactant and the product.

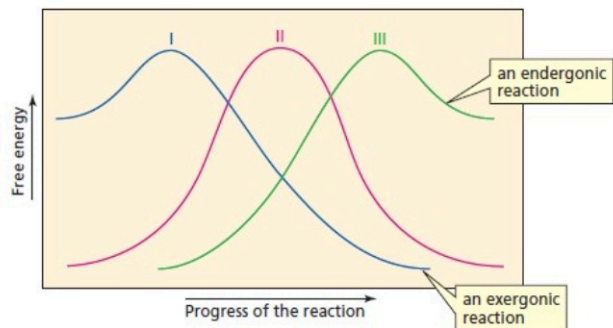


Figure 4.3 Reaction coordinate diagrams for reactions with (I) an early transition state, (II) a midway transition state, and (III) a late transition state.

Now we can understand why the tert-butyl cation is formed faster than the isobutyl cation when 2-methylpropene reacts with HCl. Because the formation of a carbocation is an endergonic reaction (Figure 4.4), the structure of the transition state will resemble the structure of the carbocation product. This means that the transition state will have a significant amount of positive charge on a carbon. We know that the tert-butyl cation (a tertiary carbocation) is more stable than the isobutyl cation (a primary carbocation). The same factors that stabilize the positively charged carbocation product stabilize the partially positively charged transition state.

Therefore, the transition state leading to the tert-butyl cation is more stable than the transition state leading to the isobutyl cation. Because the amount of positive charge in the transition state is not as great as the amount of positive charge in the carbocation product, the difference in the stabilities of the two transition states is not as great as the difference in the stabilities of the two carbocation products (Figure 4.4).

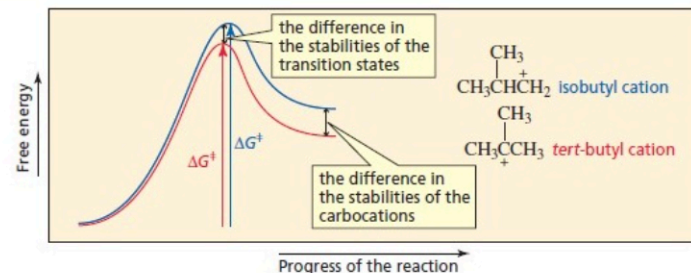
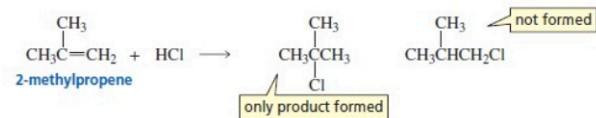


Figure 4.4 Reaction coordinate diagram for the addition of H⁺ to 2-methylpropene to form the primary isobutyl cation and the tertiary tert-butyl cation.

We have seen that the rate of a reaction is determined by the free energy of activation, which is the difference between the free energy of the transition state and the free energy of the reactant (Section 3.7). The more stable the transition state, the smaller is the free energy of activation, and therefore, the faster is the reaction. Because the free energy of activation for the formation of the tert-butyl cation is less than that for the formation of the isobutyl cation, the tert-butyl cation will be formed faster. Thus, in an electrophilic addition reaction, the more stable carbocation will be the one that is formed more rapidly. Because the formation of the carbocation is the rate-limiting step of the reaction, the relative rates of formation of the two carbocations determine the relative amounts of the products that are formed. If the difference in the rates is small, both products will be formed, but the major product will be the one formed from reaction of the nucleophile with the more stable carbocation. If the difference in the rates is sufficiently large, the product formed from reaction of the nucleophile with the more stable carbocation will be the only product of the reaction. For example, when HCl adds to 2-methylpropene, the rates of formation of the two possible carbocation intermediates—one primary and the other tertiary—are sufficiently different to cause tert-butyl chloride to be the only product of the reaction.



PROBLEM 3

For each of the following reaction coordinate diagrams, tell whether the structure of the transition state will more closely resemble the structure of the reactants or the structure of the products:

