Objective

After completing this section, you should be able to use the Hammond postulate to explain the formation of the most stable carbocation during the addition of a protic acid, HX, to an alkene.

Key Terms

Make certain that you can define, and use in context, the key term below.

• Hammond postulate

Now, back to transition states. Chemists are often very interested in trying to learn about what the transition state for a given reaction looks like, but addressing this question requires an indirect approach because the transition state itself cannot be observed. In order to gain some insight into what a particular transition state looks like, chemists often invoke the Hammond postulate, which states that a transition state resembles the structure of the nearest stable species. For an exergonic reaction, therefore, the transition state resembles the reactants more than it does the products.

If we consider a hypothetical exergonic reaction between compounds A and B to form AB, the distance between A and B would be relatively large at the transition state, resembling the starting state where A and B are two isolated species. In the hypothetical endergonic reaction between C and D to form CD, however, the bond formation process would be much further along at the TS point, resembling the product.
The Hammond Postulate is a very simplistic idea, which relies on an assumption that potential energy surfaces are parabolic. Although such an assumption is not rigorously true, it is fairly reliable and allows chemists to make energetic arguments about transition states by employing arguments about the stability of a related species. Since the formation of a reactive intermediate is very reliably endergonic, arguments about the stability of reactive intermediates can serve as proxy arguments about transition state stability.

The Hammond Postulate and the S\textsubscript{N}1 Reaction

the Hammond postulate suggests that the activation energy of the rate-determining first step will be inversely proportional to the stability of the carbocation intermediate. The stability of carbocations was discussed earlier, and a qualitative relationship is given below:

\[
\begin{align*}
\text{Carbocation} & \quad \text{Stability} \\
\text{CH}_3^+ & < \text{CH}_3\text{CH}_2^+ < (\text{CH}_3)_2\text{CH}^+ \approx \text{CH}_2=\text{CH}-\text{CH}_2^+ < \text{C}_6\text{H}_5\text{CH}_2^+ \approx (\text{CH}_3)_3\text{C}^+
\end{align*}
\]

Consequently, we expect that 3º-alkyl halides will be more reactive than their 2º and 1º-counterparts in reactions that follow an S\textsubscript{N}1 mechanism. This is opposite to the reactivity order observed for the S\textsubscript{N}2 mechanism. Allylic and benzylic halides are exceptionally reactive by either mechanism.

Exercises

Questions

Q7.10.1

Consider the second step in the electrophilic addition of HBr to an alkene. Is this step exergonic or endergonic and does the transition state represent the product or the reactant (cation)? Draw out an energy diagram of this step reaction.

Solutions

S7.10.1
Exergonic and the transition state (second step) represents the reactant (cation).

As shown to go from intermediate cation to final product the step is exergonic.

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