Answers to Problem 79, Chemistry 301X - 2006

Consider the addition of HBr to 1-butene. One of the two “possible” products is formed exclusively. Explain why.

Oopsie - I’ll bet you said that the secondary carbocation is far more stable than the putative primary carbocation and is thus formed preferentially.

What have the products (the two ions) to do with the rates of their formations?

Ans: nothing direct.

So carefully modify your answer (get it checked!), and explain the relevance to it of the Hammond Postulate.

In the TS for formation of the secondary carbocation, that secondary carbocation will be partially formed - there will be a partial positive charge on the secondary carbon.

In the TS for formation of the primary carbocation, that primary carbocation will be partially formed - there will be a partial positive charge on the primary carbon.

If a fully formed secondary carbocation is more stable than a fully formed primary carbocation, a partially formed secondary carbocation will be more stable than a particlly formed primary carbocation.

Hence the TS for formation of the secondary carbocation will be more stable than the TS for formation of the primary carbocation.

Both possible protonations will be highly endothermic. Thus, the intermediate carbocations will be decent models for the transition states. “For an endothermic reaction, the TS will resemble the products.”