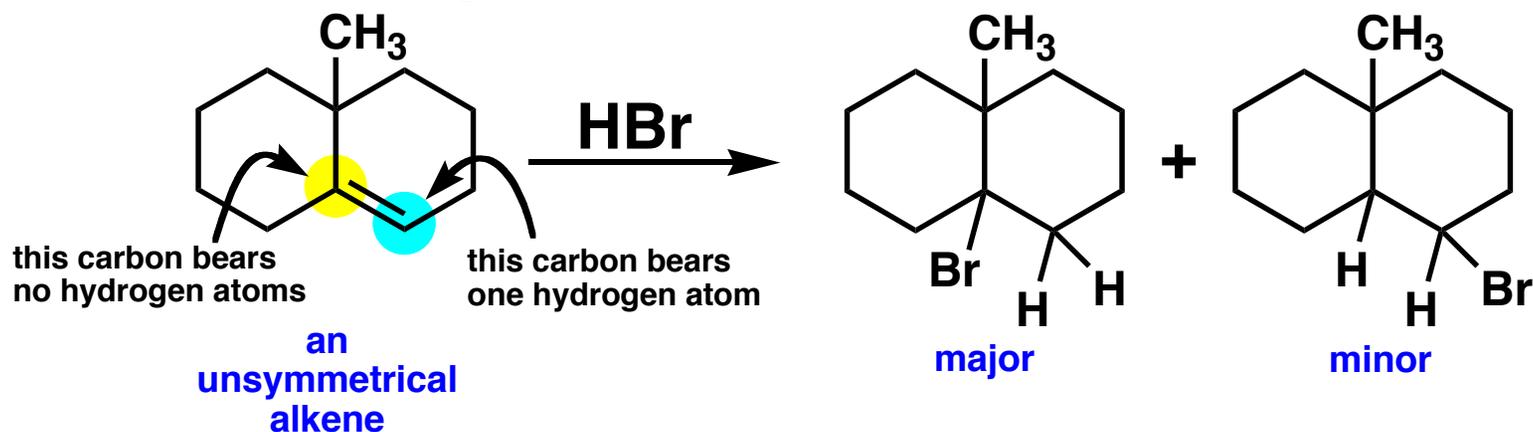


Unsymmetrical Alkenes



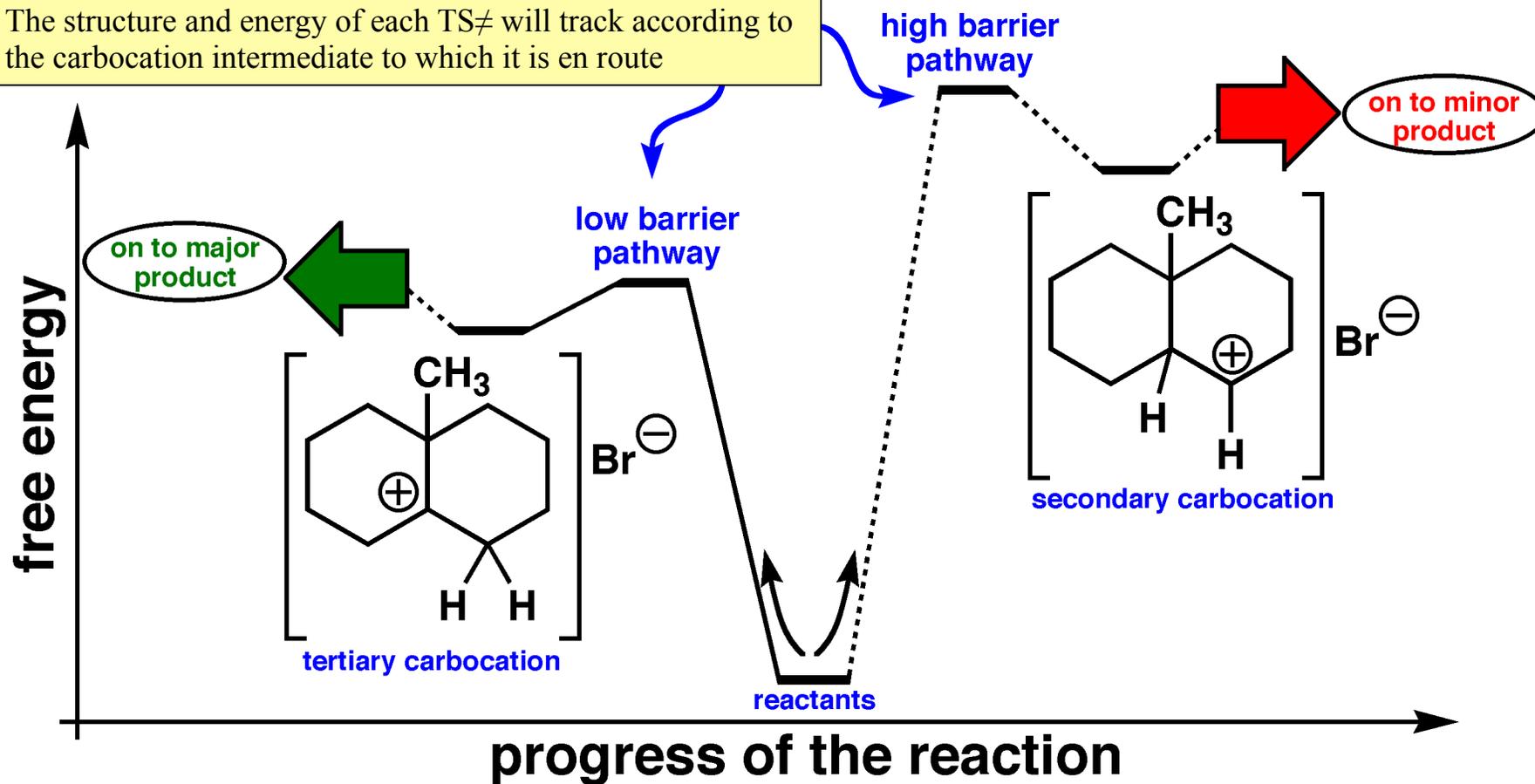
The first step of the mechanism involves the formation of a carbocation intermediate. Because the alkene is unsymmetrical, there are two possible carbocations that can form. The relative stability of these carbocation intermediates (technically, the transition state leading to these intermediates) determines which product is formed the fastest. **Hammond's postulate** allows us to predict the relative energy of the TS^\ddagger s leading to the two possible intermediates. Draw a representation of the transition state structures for both modes of reactivity. Your representations should show that one begins to develop character of a **secondary carbocation**, while the other develops character of a **tertiary carbocation**. The TS^\ddagger leading to the secondary carbocation is a higher energy species compared to the TS^\ddagger leading to the tertiary carbocation intermediate. Thus, the secondary carbocation pathway represents a higher barrier to reaction. In contrast, the TS^\ddagger leading to the tertiary carbocation is a lower energy species, and thus represents a lower barrier to the reaction pathway. The reaction coordinate diagram illustrates this logic and helps explain why the major observed product results from attack of bromide on a tertiary carbocation. Start from the reactants. Notice the pair of diverging pathways, one leading to the major product and the other leading to the minor product.



Diverging Reaction Pathways

The *relative* energies of these TS \neq can be determined because:

- 1) Both steps are examples of a “late” TS \neq
- 2) The structure and energy of each TS \neq will track according to the carbocation intermediate to which it is en route



Electrophilic addition to alkenes

Stereospecific addition

Epoxidation peracid

Diels-Alder reactions

Unsymmetrical alkenes HBr

Nucleophilic substitution

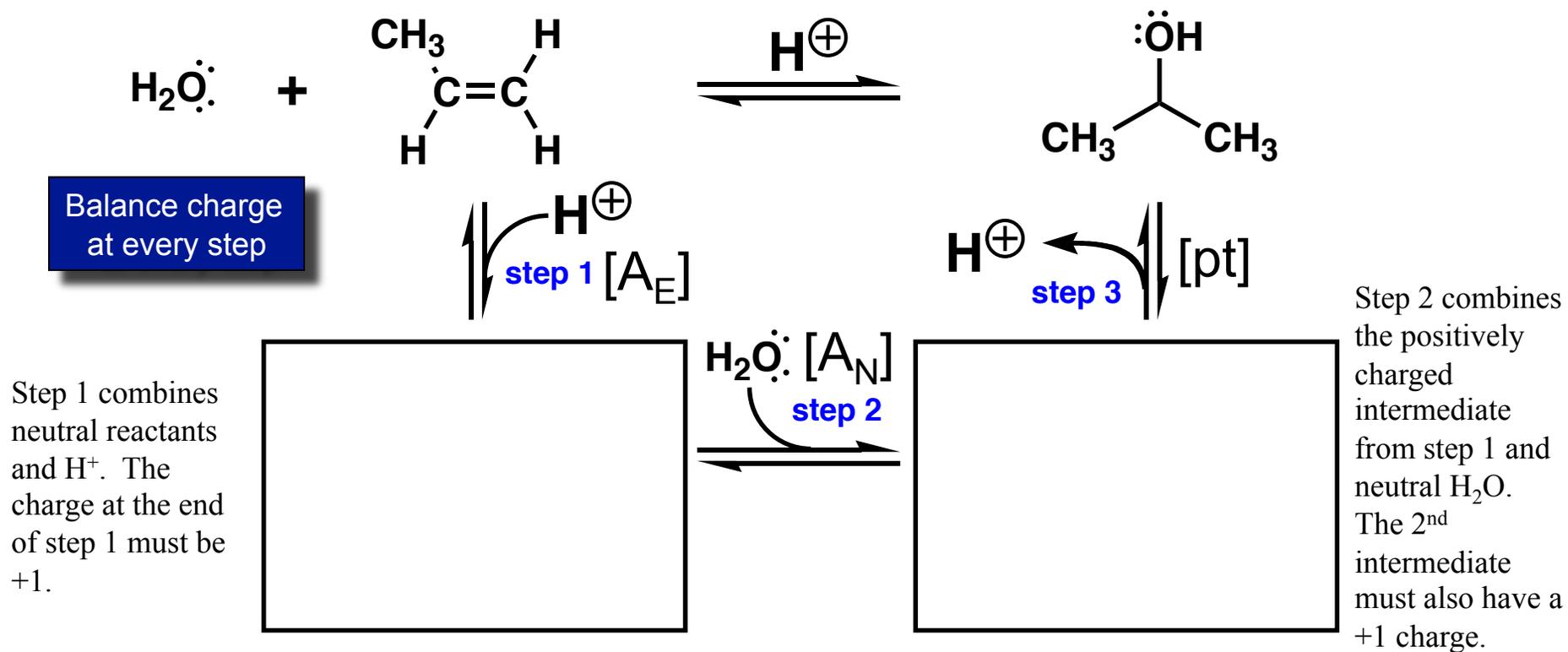
Regioselective addition

Elimination

Diene bromination

<http://www.chemtube3d.com/>

Acid-Catalyzed Addition of Water or Alcohols to Alkenes



Notice first, that the stoichiometry is balanced. Water is probably the solvent of this reaction, and in this case, it participates in the reaction, too. Such behavior where the solvent gets incorporated into the product is fairly common in organic chemistry. In contrast to water, the H⁺ above the equilibrium arrow does not enter into the stoichiometry. However, H⁺ does play an important role. If you were to combine water and an alkene without any acid, no change will take place for a long time, at least not at lower temperatures. These observations point to the notion that the reaction is catalyzed by H⁺, meaning that acid enhances the rate of the reaction, but does not show up in the stoichiometry. So, when you see H⁺ or HO⁻ listed above the arrow, but not enter the stoichiometry, think about acid or base catalyzed reactions. Complete the mechanism, reasoning by analogy to the [A_DE₂] mechanism for H-Br addition to an alkene.