EA3. Solvent Participation in Electrophilic Addition

Alkenes can donate their electrons to strong electrophiles and the resulting carbocations combine with the counterion of the electrophile to undergo an overall addition reaction. However, there may be some cases in which the counterion does not combine with the carbocation.

Hydrobrominations of the type we have looked at only occur under certain conditions. Other conditions can lead to other products. For example, a solvent such as water can also participate in the reaction. The oxygen-based cation (or oxonium ion) that results can easily lose its charge through loss of a proton. As a result, a molecule of water adds to the alkene overall. The alkene becomes an alcohol. This reaction is called an "acid-catalyzed hydration" of an alkene.

Problem EA3.1.

Explain how the hydration of an alkene in the presence of acid is a catalytic reaction.

Problem EA3.2.

In many cases, equilibrium mixtures of multiple products may result from the addition of acids to alkenes. Show mechanisms, with curved arrows, for the following reactions.

1. The conversion of 2-butene to 2-chlorobutane with aqueous HCl.
2. The conversion of 2-butene to 2-butanol with aqueous HCl.
3. The conversion of 2-chlorobutane to 2-butene with aqueous HCl.
4. The conversion of 2-butanol to 2-butene with aqueous HCl.

On the other hand, in the absence of any solvent, the bromide ion might still have some competition in the second step. The neat reaction (neat means "without solvent" of an alkene with a small amount of acid can result in polymerization. The alkene, which acted as a nucleophile in the first step, can also act as a nucleophile in the second step.

It is important to remember that in any reaction, millions of molecules are involved. Even if one alkene molecule reacts with acid in the first step of a reaction, there are still plenty of other alkene molecules around to act as nucleophile in the second step.
Problem EA3.3.

Provide a mechanism for the polymerization shown above. Assume there are four 2-methylpropene molecules and one hydrogen bromide molecule to begin.

Problem EA3.4.

Chain reactions involve an *initiation step*, in which a reactive species is generated; *propagation steps*, in which the reactive species reacts to make a new reactive species; and a *termination step*, in which the reactive species reacts to make a stable molecule. Label each of the steps in your mechanism from the previous question.

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