Difference Between Markovnikov and Anti-Markovnikov Rule

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Key Difference - Markovnikov vs Anti-Markovnikov Rule

In the early 1870s, a Russian chemist named Vladimir Markonikov derived a rule based on a series of empirical observations. The rule was published as the Markovnikov's rule. **The Markovnikov's rule helps to predict the resulting formula of alkane, when a compound having the general formula of HX (HCl, HBr or HF) or H_2O is added to an asymmetric alkene (such as propane). It is possible to reverse the minor and major products when the reaction conditions are changed, and this process is referred to as Anti-Markovnikov addition.** The **key difference** between Markovnikov rule and the anti-Markovnikov rule is explained below.

What is Markovnikov Rule?

The definition of Markovnikov rule is, when the addition of protic acid with the formula of HX (where X= halogen) or H_2O (considered as H-OH) to an alkene, hydrogen attaches to the double bonded carbon with the greater number of hydrogen atoms, while the halogen (X) attaches to the other carbon. Therefore, this rule is often interpreted as 'the rich get richer'. The rule can be illustrated using the reaction of propene with hydrobromic acid (HBr) as follows.

Figure 01: Markovnikov's Rule is illustrated by the reaction of Propene with Hydrobromic Acid

The same rule is applied when an alkene reacts with water to form alcohol. The hydroxyl group (-OH) adds to the double-bonded carbon with the greater number of C-C bonds, while the hydrogen atom (H) adds to the other double bonded carbon that has more C-H bonds. Therefore, according to Markovnikov rule, when an HX is added to an alkene, the major product has H atom in the less substituted position while the X in the more substituted position. Therefore, this product is stable. However, it is still possible to form a less stable product, or we call it a minor product, in which H atom bonds to more substituted position of the C=C bond, while X bonds to the less substituted position.

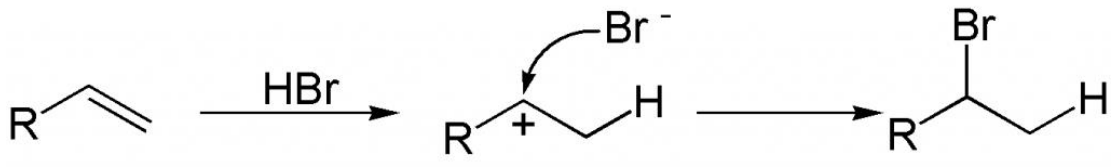

Figure 02: Hydrogen Bromide addition to an Alkene

The mechanism of the addition of HX to an alkene can be explained in two steps (See fig 02). First, the addition of a proton (H^+) is taken place as the C=C double bond of alkene reacts with H^+ of HX (in this case it's HBr) to form a carbonation intermediate. Then reaction of an electrophile and a nucleophile is taken place as the second step to form a new covalent bond. In our case, Br^- reacts with carbonation intermediate which is positive in charge to form the final product.

What is Anti-Markovnikov Rule?

Anti- Markovnikov rule explains the opposite of the original statement of Markovnikov's rule. When HBr is added to an alkene in the presence of peroxide, H atom bonds to double-bonded carbon that has less C-H bonds, while Br bonds to the other carbon that has more C-H bonds. This effect is also known as Kharash effect or peroxide effect. The anti-Markovnikov addition also takes place when reactants are exposed to ultraviolet light. This is the exact opposite of Markovnikov rule. However, the anti-Markovnikov rule is not the exact reverse process of Markovnikov addition as the mechanisms of these two reactions are entirely different.

Markovnikov reaction is an ionic mechanism, whereas anti-Markovnikov reaction is a free-radical mechanism. The mechanism takes place as a chain reaction and has three steps. The first step is the chain-initiating step, where photochemical dissociation of HBr or peroxide is taken place to form Br and H free radicals. Then in the second step, Br free radical attacks the alkene molecule to form two possible bromoalkyl free radicals. 2° free radical is more stable and formed predominantly.

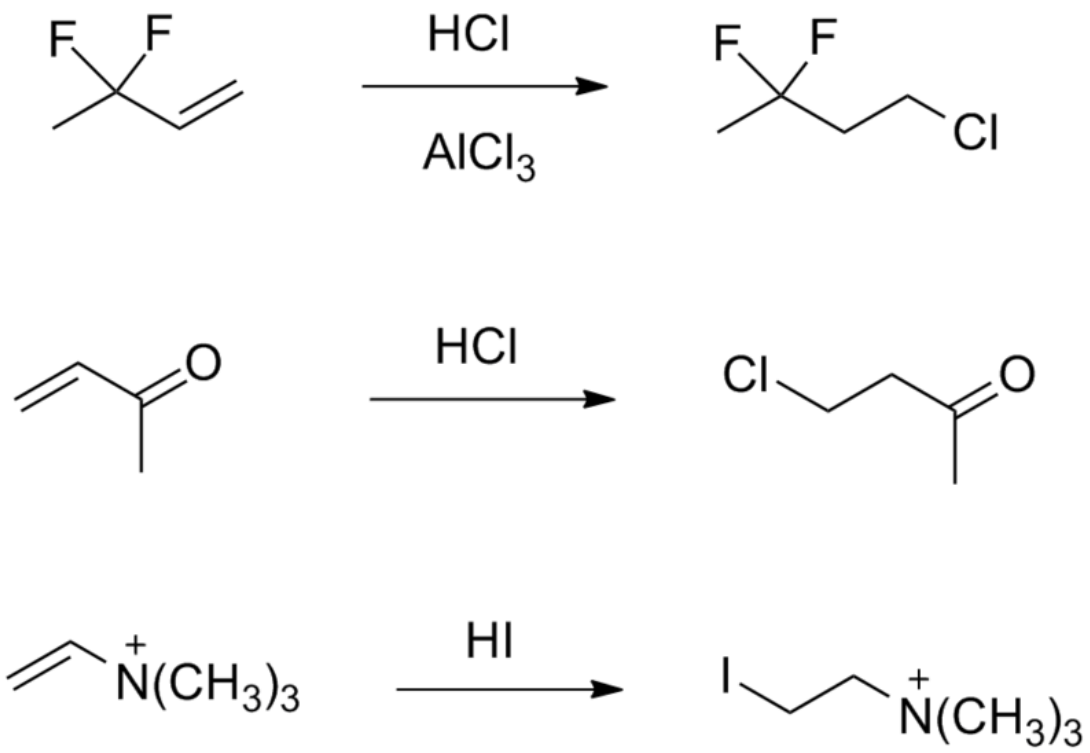

Figure 3: Anti- Markovnikov Addition Examples

During the final step, the more stable bromoalkyl free radical reacts with HBr forming anti-Markovnikov product plus another bromine free radical, which continuous the chain reaction. Unlike HBr, HCl and HI do not result in anti-Markovnikov products as they do not undergo free radical addition reaction. It is because H-Cl bond is stronger than H-Br bond. Even though H-I bond is much weaker, the formation of I_2 is more preferred as C-I bond in relatively unstable.

What is the Difference Between Markovnikov and Anti Markovnikov Rule?

Markovian Rule vs Anti Markovian Rule	
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Mechanism	
ionic mechanism	free radical mechanism
Reactants	
HCl, HBr, HI or H_2O	only HBr (not HCl or HI undergo this addition reaction)

Medium/Catalyst	
no medium is required	peroxide or ultraviolet must be present

Summary - Markovnikov vs Anti-Markovnikov Rule

Markovnikov and anti-Markovnikov are two types of addition reactions occurring between HX (HBr, HBr, HI and H_2O) and alkenes. Markovnikov reaction occurs when the addition of HX to an alkene, where H bonds to less substituted carbon atom of the double bond, while X bonds to the other double bonded carbon atom through an ionic mechanism. The anti-markovnikov reaction takes place when HBr (not HCl, HI or H2O) is added to an alkene, where Br bonds to less substituted double-bonded carbon, while H bonds to the other carbon atom, through a free radical mechanism. This is the difference between Markovnikov and Anti-Markovnikov Rule.

Reference:

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