The addition reaction of a hydrogen halide molecule, such as HCl or HBr, to an alkene produces an alkyl halide as a product. This process is known as a Hydrohalogenation reaction. Figure 3.2.1.a. Addition reaction of the hydrogen halide HCl to an alkene Figure 3.2.1.b. Addition reaction of the hydrogen halide HBr to an alkene The mechanism (Figure 3.2.1.c.) for hydrohalogenation is a two-step process. In the first step, the alkene is protonated by HBr, resulting in a carbocation intermediate and a halide anion (such as Br–). In this protonation step, the π bond is broken to allow for formation of a sigma bond to the proton. This results in a carbon that loses π electron density and becomes cationic. In the second step, the halide ion formed in the first step acts as a nucleophile to attack the electrophilic carbocation intermediate. The result of the second step is that a new C–Br σ bond is formed. Recall that in addition reactions, one π bond and one σ bond are broken, and two σ bonds are formed. In this mechanism, the first step involves breaking the H–Br σ-bond and the C=C π-bond and forming a new C–H σ-bond, while the second step involves forming a new C–Br σ bond. In addition, the hybridization at carbon changes: the C=C double bond of reactants have sp2 hybridized carbon atoms, which become sp3 hybridized in the products. This reaction mechanism has some similarities with the SN1 mechanism discussed in Chapter 3.1.3. For example, hydrohalogenation and unimolecular nucleophilic substitution (SN1) are similar in that both mechanisms occur in two steps and involve a carbocation intermediate. In addition, the second step of both mechanisms is identical: the electrophilic carbocation is attacked by the nucleophilic halide to form a new C–X bond. SN1 reactions and hydrohalogenation differ in the first step of the reaction: an SN1 mechanism involves loss of a leaving group, whereas an alkene has no leaving group and instead is protonated in the first step. Figure 3.2.1.c. Mechanism of hydrohalogenation addition reaction to a symmetric alkene. The nucleophilic π electrons in the alkene attack the electrophilic proton, breaking the H–Br bond and forming a new C–H bond, resulting in a carbocation intermediate. After the breaking of the π bond, one of the carbon atoms has only 3 bonds and becomes cationic. The anionic, nucleophilic bromide can then attack the carbocation and form a new C–Br bond. In the above examples, the alkenes are symmetrical in structure, with each alkene carbon existing in identical bonding environments. As a result. it is observed that there is no preference between which atom the halide or hydrogen atom are added to This is because the reaction pathway will proceed via an identical carbocation intermediate, so there is no preference on which side the C–H vs. C–X bond is formed, and the final product will be the same. Figure 3.2.1.d. Hydrohalogenation of symmetrical alkenes yields the same carbocation intermediate and the same product. For an asymmetrical alkene, where the double bonded carbons atoms have different substituents, the placement of the H and X atoms across the π bond is critical. For example, in the following reaction (Figure 3.2.1.e.), two possible products could be produced: 1-bromo-1-methylcyclohexane and 1-bromo-2-methylcyclohexane. Experimental observations demonstrate that 1-bromo-1-methylcyclohexane is the main product for the reaction. To explain and understand the outcome of the reaction, we need to consider the mechanism of the reaction and the stability of the intermediates formed. Figure 3.2.1.e. Hydrohalogenation of 1-methylcyclohexene yields two possible products. The major product is 1-bromo-1-methylcyclohexane; the minor product is 1-bromo-2-methylcyclohexane. In reactions where multiple products can form, the product that is formed in over 50% of the theoretical yield is referred to as the major product. This distribution in products is due to the energy required to form it. The major product requires less energy to form, so more will form per unit time. In reactions where multiple products can form, the product that is formed in less than 50% of the theoretical yield is referred to as the minor product. This distribution in products is due to the energy required to form it. The minor product requires more energy to form, so less will form per unit time. When the nucleophilic π bond attacks the electrophilic proton from H–X, a carbocation intermediate is formed. Recall carbocation stability (see Chapter 3.1.3): higher substituted carbocations are the most stable due to greater neighbouring electron density stabilization, while lowly substituted carbocations are less stable due to a lack of neighbouring electron density available to provide charge dissipation. The energy profile diagram for the hydrohalogenation of symmetric alkenes is shown below: Figure 3.2.1.f. Energy profile diagram for the hydrohalogenation reaction of the symmetric alkene, cyclohexene. The 2 maxima represent the two steps of the reaction. The first step (protonation of the alkene) is the slow step, hence the greater activation energy. The second step (nucleophilic attack of the carbocation by bromide) requires less energy and is therefore faster. The first step of the reaction, protonation of the alkene, yields the carbocation intermediate. Since the carbocation intermediate is unstable and high in potential energy, there is a large activation barrier associated with this step resulting in it being the rate limiting step. The second step, nucleophilic attack of the carbocation by bromide, results in the final alkyl halide product. Since the first step of the addition mechanism is rate limiting, we will focus on it to justify the differences in product formation. Just as carbocation stability is important when discussing the unimolecular nucleophilic substitution (SN1) mechanism, so too does it play a role in the hydrohalogenation mechanism (Figure 3.2.1.g). The first step of the hydrohalogenation mechanism adds a new C–H bond to one carbon atom and a formal positive charge to the other carbon atom (the carbocation). When looking at the possible carbocation intermediates formed, if the C–H bond was created on the more substituted carbon (tertiary position), then a secondary carbocation would form on the other carbon atom, leading to the 1–bromo–2–methylcyclohexane product (Figure 3.2.1.g, bottom). On the other hand, if the C–H bond was created on the less substituted carbon (secondary position), then a tertiary carbocation is formed on the other carbon atom, leading to the 1–bromo–1–methylcyclohexane product (Figure 3.2.1.g, top). Since a tertiary carbocation intermediate is more stable than a secondary carbocation intermediate, the tertiary carbocation intermediate will have a smaller activation energy barrier associated to its formation, and will form faster. As a result, more tertiary carbocation intermediate produced per unit time result in more alkyl halide product produced per unit time, leading to a higher abundance of 1-bromocyclohexane (major product). Therefore, when performing hydrohalogenation reactions to alkenes, the electrophilic hydrogen atom is added to the least substituted carbon because it results a more substituted and more stable carbocation The halide will then attack the more substituted position in the second step of the reaction. This reaction is said to be regioselective – there is a preference to which carbon atoms the hydrogen and halide form sigma bonds too. In this case, we call this Markovnikov regioselectivity , named after Vladimir Markovnikov who studied alkene addition reactions extensively in the mid 1800s. As a result, we apply something known as Markovnikov’s rule to hydrohalogenation reactions, which states that the carbon that is already bonded to more hydrogen atoms (less highly substituted position) gets the hydrogen. This rule is also cleverly coined as the “rich get richer” rule, where a carbon atom with more hydrogen atoms bonded to it is considered “rich”. Regioselectivity is when a reaction mechanism favours bond formation at a particular atom over other possible atoms. For alkene additions, we observe two types of regioselectivity – Markovnikov and Anti-Markovnikov. A Markovnikov regioselective product results from a mechanism that would result from the more stable of two possible carbocation intermediates. An Anti-Markovnikov regioselective product results from a mechanism that would result from the less stable of two possible carbocation intermediates. Figure 3.2.1.g. Hydrobromination of 1–methylcyclohexene. The π electrons in the alkene attack the electrophilic hydrogen, breaking the H-Br bond. This causes a new C–H bond to be formed. On the top pathway, the new C–H bond is formed on the less substituted carbon, generating a tertiary carbocation on the more substituted carbon. On the bottom pathway, the new C–H bond is formed on the more substituted carbon, generating a secondary carbocation on the less substituted carbon. In the second step, the nucleophilic bromide anion attacks the carbocation. This yields two products: a major (Markovnikov) product (top pathway) and a minor product (bottom pathway). (The full solution to this problem can be found in Chapter 5.2) Another way of naming the major and minor product of a reaction when there is Markovnikov regioselectivity is the Markovnikov and Anti-Markovnikov products. Figure 3.2.1.h. Hydrobromination of 1–methylcyclohexene yields two products: 1–bromo–1–methylcyclohexane, the Markovnikov product, and 1–bromo–2-methylcyclohexane, the Anti-Markovnikov product. The Markovnikov product is formed through a lower energy pathway, where a more stable tertiary carbocation intermediate is formed, and the hydrogen atom is added to the carbon bonded to more hydrogens. The Anti-Markovnikov product is formed through a higher energy pathway, where a less stable secondary carbocation intermediate is formed, and the hydrogen atom is added to the carbon bonded to less hydrogens. The energy profile diagram for the hydrohalogenation of alkenes is shown below (Figure 3.1.2.i). Figure 3.2.1.i. Energy profile diagram for the electrophilic addition of HBr to 1–methylcyclohexene. The 2 maxima represent the two steps of the reaction. The first step (protonation of the alkene) is the slow step, hence the greater activation energy. The second step (nucleophilic attack of the carbocation by bromide) requires less energy and is therefore faster. The blue pathway is higher in energy because the secondary carbocation intermediate is less stable; the green pathway is lower in energy because the tertiary carbocation intermediate is more stable. The two maxima represent the two steps of the reaction, where the first step (protonation of the alkene) is the rate-limiting step. Carbocation stability dictates which product is formed: the more highly substituted the carbocation, the more stable it will be, and the reaction pathway that involves the more stable carbocation will require less energy to overcome the activation energy barrier and proceed faster. (The full solution to this problem can be found in Chapter 5.2) The following video includes a worked example from a previous CHEM 1AA3 test or exam that students struggled with. Try solving it on your own before looking at the solution. Hydrohalogenation is a reaction using an alkene and a hydrogen halide (HX) as reactants, where the hydrogen and halogen are added to each alkene carbon The mechanism involves two steps, the first being rate limiting: Step 1: The π electrons of the double bond nucleophilically attack the proton and form a σ bond to it, creating a carbocation and a halide as intermediates Step 2: The halide nucleophilically attacks the carbocation, creating the product: an alkyl halide If the alkene is asymmetrical, then there’s two possible products: major and minor Because of the carbocation stability, the more substituted carbocation intermediate will be the intermediate that leads to the major product The major product is also called the Markovnikov product, while the anti–Markovnikov product is also the minor product Key terms in this chapter: Key term Definition Hydrohalogenation reaction The addition reaction of a hydrogen halide to an alkene. This produces an alkyl halide as a product. Any feedback or comments on this chapter? You may either email chemoer@mcmaster.ca, access this MS Form, or provide a comment in the feedback box below. definitionThe addition reaction of a hydrogen halide to an alkene. This produces an alkyl halide as a product. Alkenes are compounds that contain at least one carbon-carbon double bond. Because of the reactivity of the pi bonds within the structure of the compound, alkene can undergo a variety of addition reactions. One of the most common addition reactions for alkene is hydrohalogenation. Hydrohalogenation is a type of addition reaction of alkene where an H and X atom is added to the unsaturation site on the alkene structure. The process involves reacting alkene with HX (where X = Cl, Br, or I). The H and X are added across the pi bond. An example of this process is shown below. The process of addition proceeds by firs having the proton attack one of the carbons of the pi bond. Because of these, electron rearrangement leads to production of a carbocation. The carbocation is then attacked by the negatively charged anion (X-). The specific mechanism for the reaction is shown below. Hydrohalogenation reaction is relatively simple for symmetrical alkenes. However, there are special considerations for asymmetrical alkenes. In 1869, Vladimir Markovnikov, developed a rule applied to addition reactions based on his observations. The rule states that the hydrogen atom attaches itself to the less substituted carbon (vinyllic position containing the larger number of hydrogen atoms). The X atom on the other hand is attached to the more substituted carbon. Following Markovnikov Rule, it is observable that it involves formation of the more stable carbocation. Because of having a more stable carbocation, the process of adding the nucleophile X- will require less energy. The lower energy barrier of formation of a tertiary carbon compared to a secondary carbon results to a faster reaction. This tutorial is all about the hydrohalogenation of alkenes—breaking down the reaction mechanism, Markovnikov’s rule, and those pesky carbocation rearrangements that always seem to complicate things. So, grab a cup of coffee, pull out your notebook, and let’s dive in. Hydrohalogenation is a reaction where an alkene reacts with a hydrogen halide (HX), where X is typically chlorine, bromine, or iodine. During this reaction, one carbon of the alkene receives a hydrogen, while the other carbon gets the halide. To understand this, let’s consider a generic alkene with two carbons, labeled carbon 1 and carbon 2. The double bond in the alkene acts as a nucleophile, meaning its electrons are attracted to the positively charged hydrogen in the HX molecule. The hydrogen-halide bond in HX is highly polarized—bromine, for example, is very electronegative, pulling electron density away from the hydrogen, making it highly electrophilic. Since we have a nucleophile (the alkene) and an electrophile (HX), they react. This first step is called the electrophilic attack because the alkene’s electrons attack the hydrogen. When the alkene donates electrons to form a new bond with the hydrogen, the pi bond breaks, leaving the other carbon electron-deficient—creating a carbocation. Meanwhile, the halide (X^-) is now free in solution as a negatively charged ion. At this stage, we have a highly reactive carbocation, which is electrophilic because it is electron-deficient. The negatively charged halide (Br^-, Cl^-, etc.) then acts as a nucleophile and attacks the carbocation, forming a new bond. This step is called the nucleophilic attack, and it gives us our final product: a molecule where the hydrogen is attached to one carbon and the halide is attached to the other. Let’s apply this to a real molecule—1-methylcyclohexene. Here, we again label our carbons as carbon 1 and carbon 2. The double bond serves as a nucleophile, attacking the hydrogen from HBr, while the electrons from the HBr bond return to bromine, forming Br^-. Now, we have a choice. Either carbon 1 or carbon 2 can receive the hydrogen. If carbon 1 gets the hydrogen, a carbocation forms on carbon 2, and if carbon 2 gets the hydrogen, the carbocation forms on carbon 1. The key here is carbocation stability: • A tertiary carbocation (three carbon attachments) is more stable than a secondary carbocation (two carbon attachments), which is more stable than a primary carbocation (one carbon attachment). • A methyl (CH_3^+) carbocation is extremely unstable and practically non-existent in nature. Since a tertiary carbocation is more stable than a secondary carbocation, the reaction favors the pathway that produces the more stable intermediate. This observation was formulated by Vladimir Markovnikov in the 19th century, known as Markovnikov’s rule. The rule states that in hydrohalogenation reactions, the hydrogen adds to the less substituted carbon (the one with fewer carbon attachments), while the halide attaches to the more substituted carbon (the one with more carbon attachments). This ensures the formation of the most stable carbocation. Interestingly, Markovnikov originally noticed cases where the halide sometimes ended up on unexpected positions in the molecule. He had no idea why—because at the time, carbocations hadn’t been discovered! Today, we know that carbocation rearrangements are responsible for these unexpected results. Let’s consider an example where rearrangement occurs. In a typical reaction, the first step is still the electrophilic attack, where the double bond donates electrons to the hydrogen, forming a carbocation. If the initial carbocation isn’t as stable as a nearby alternative, a rearrangement can occur. For example, if we form a secondary carbocation adjacent to a tertiary carbon, the system can stabilize by shifting a nearby hydrogen (along with its bonding electrons) to the carbocation site. This is called a 1,2-hydride shift, and it results in the formation of a more stable tertiary carbocation. Once the carbocation has stabilized, the halide (X^-) can attack, forming the final product. If you didn’t account for the rearrangement, you’d expect a different product! But because carbocations always seek out the most stable configuration, the major product follows this rearranged pathway. In some cases, we have to decide between multiple possible carbocations. If one of them is benzylic—meaning it is adjacent to a benzene ring—it will be resonance stabilized, making it much more favorable than a typical secondary or tertiary carbocation. These resonance effects can often override even Markovnikov’s rule in determining the final product. By considering these rules—Markovnikov’s rule, carbocation stability, and possible rearrangements—we can accurately predict the outcome of hydrohalogenation reactions. Last updated: March 5th, 2025 | Hydrohalogenation of Alkenes and Markovnikov’s Rule When hydrohalic acids (HCl, HBr, HI) are added to alkenes, addition reactions can occur, resulting in formation of a C-H and C-halogen bond and breakage of a C-C pi bond. The reaction tends to occur such that the halogen ends up attached to the carbon of the alkene attached to the fewest hydrogen atoms, a phenomenon known as Markovnikov’s Rule. Addition of H-X to alkenes occurs through a protonation of the alkene to give a carbocation intermediate, followed by addition of the halide to the carbocation. A better reformulation of Markovnikov’s rule is therefore that addition of HX to alkenes will proceed through the most stable carbocation, which is generally the more substituted carbon of the alkene. (Note that H-Br with peroxides (RO-OR) operates through a different reaction mechanism – see Free Radical Addition of H-Br to Alkenes). Carbocation rearrangements (hydride or alkyl shifts) can occur if they will result in a more stable carbocation intermediate. H-X will also add to alkynes (See: Addition of HX to alkynes) and dienes (See: 1,2- and 1,4- Addition of HX To Dienes) but will not add to aromatic rings. Table of Contents 1. Reaction of Alkenes With Hydrohalic Acids (HCl, HBr, HI) When alkenes are treated with hydrohalic acids (HCl, HBr, or HI) they form alkyl halides. This is sometimes called hydrohalogenation of alkenes since it results in the addition of hydrogen and a halogen. In these addition reactions: the C-C pi bond and the H-X bond breaks; a new C-H and C-X bond forms (where X is Cl, Br, or I). If we add up the bond dissociation energies (BDE’s) of the bonds that form (C-H, about 98 kcal/mol, and C-Cl, about 81 kcal/mol) and subtract their sum from those of the bonds that break (C-C pi, about 60 kcal/mol, and H-Cl, about 103 kcal/mol) the reaction is exothermic by about 18 kcal/mol for the addition of HCl. [Link to a useful table] Acid is required for these reactions to occur; no addition of halide to alkenes will happen in the absence of strong acid. (In other words, HCl = , but NaCl =). The new C-halogen bond tends to form on the most substituted carbon of the alkene (i.e. the one with the fewest carbons), and the new C-H bond tends to form on the carbon of the alkene containing the most hydrogens. 2. Markovnikov’s Rule: Regioselectivity of HX Addition to Alkenes The reactions of alkenes with has been known for over 150 years. When an alkene is not symmetrical, the reaction has the potential to form two different constitutional isomers (“regioisomers”). However, in many cases, one constitutional isomer is formed in a much higher proportion than the other. In other words, the reaction is regioselective. In an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens. This has come to be known as “Markovnikov’s Rule“. Markovnikov’s rule is what we would call an “empirical” rule. It was based purely on observed results, without any real underlying understanding of the mechanism of the reaction. In later years people had a hard time replicating Markovnikov’s results with HBr, often finding that the least substituted regioisomer was formed instead! Later on, in the 1930s the cause of this aberrant regioselectivity was found to be the presence of peroxides in solvent, which led to a free-radical process for addition of H-Br to alkenes, which does not occur with H-I or H-Cl. See article – Free-Radical addition of H-Br to Alkenes. [Note 1] Subsequently we tend to say, for better or worse, that addition reactions to alkenes that follow this pattern (such as their reaction with H3O+) are “Markovnikov-selective“, whereas reactions that follow the opposite pattern are “anti-Markovnikov selective” (such as hydroboration of alkenes). See if you can apply the pattern in the reaction of the alkene below (1-methylcyclopentene) with H-Cl. Click to Flip Another example is below. Draw the major product(s) and determine how they will be related: Click to Flip Can you work backwards to come up with the best starting material for this reaction? Click to Flip 3. Stereoselectivity (Or Lack Thereof) In Addition of HX To Alkenes When addition reactions occur across an alkene pi-bond, the (sp2-hybridized) trigonal planar carbons of the alkene are converted into (sp3-hybridized) tetrahedral carbons, and with this comes the potential for formation of stereoisomers. (See article: Types of Isomers) When the two new bonds to carbon are formed on the same face of the alkene, the addition is said to be “syn“ When the two new bonds are formed on opposite faces of the alkene, the addition is said to be “anti“. Addition reactions that give primarily syn or anti products are said to be stereoselective, and we will meet many examples in subsequent articles in this chapter (e.g. halogenation is stereoselective for anti products, and hydroboration is stereoselective for syn products). Addition of H-X to alkenes gives a mixture of syn addition products and anti addition products [Note 2]. In other words, the reaction is not particularly stereoselective. This lack of stereoselectivity leads to mixtures of syn and anti addition products, in some cases each as mixtures of enantiomers. See if you can draw the products of the reaction below: Click to Flip 4. Hydrohalogenation of Alkenes: The Mechanism Markovnikov was one of the more prominent chemists of his era, but back in 1870 he didn’t know why the reaction tended to give the more substituted product. The first to really figure it out was Lucas in 1924 [Ref], based on observations that alkyl groups are more “electron releasing”. After many decades it was finally proposed that reaction goes through an intermediate carbocation. (The existence of carbocations was a fairly controversial subject until the 1930’s). In the first step, the alkene (a nucleophile) is protonated by strong acid, resulting in a new carbocation. [Note 3] Depending on where protonation occurs, two different carbocations may be formed. Being electron-poor species, carbocations are stabilized by adjacent electron-donating groups as well as by delocalization through resonance. (See article – 3 Factors Which Stabilize Carbocations). The transition state leading to the most stable carbocation will be lower in energy, which tends to be the most substituted carbocation. The arrow pushing for alkenes reacting with acids like H-X can be a little ambiguous – see Note 4. So it is ultimately this carbocation intermediate which is the underlying reason for why Markovnikov’s rule is observed. Carbocations have an empty p-orbital and readily accept a pair of electrons from whatever Lewis bases happen to be present in solution. In the second step, the best nucleophile present (which tends to be the halide ion) then attacks the carbocation, forming the alkyl halide. To reiterate: Markovnikov went to his grave not knowing this mechanism. Heck, many chemists of his time didn’t even accept that carbon was tetrahedral! So if you didn’t figure this mechanism out immediately, that’s to be expected and certainly nothing to feel bad about. The body of knowledge that is chemistry is built up of thousands of little experiments that eventually grew into the framework we have today. 5. Reaction Energy Diagram For Alkene Hydrohalogenation Sometimes it can be helpful to trace out the energy profile of a reaction as it progresses from starting material to products. In these diagrams, peaks (local maxima) are transition states and valleys (local minima) are intermediates. A simple hydrohalogenation reaction has two steps – each of which has a transition state – and a single carbocation intermediate. In the first step, our intrepid alkene is protonated by strong acid, resulting in the high-energy transition state TS 1. This step has the highest activation energy (the barrier between reactants and transition state) making it the rate-determining step for this reaction. From the transition state (TS1) energy maximum, the reaction proceeds to the carbocation intermediate. The second step involves attack of the halide nucleophile on the carbocation, which proceeds through transition state 2 (TS2). Note that the activation energy for this step is considerably less than for protonation of the alkene – in other words, it will be the fast step. The reaction then proceeds through TS2 to give the final product, the alkyl halide. 6. Carbocation Rearrangements – Hydride and Alkyl Shifts One key to the proposal of a carbocation intermediate was the observation that some hydrohalogenation reactions give products of carbocation rearrangements in addition to the expected addition product. For example when 4-methyl-1-butene was treated with HCl and allowed to sit at room temperature for an extended period, the product mixture was found to contain about half the expected Markovnikov addition product in addition to a new tertiary alkyl halide. [Ref] In this reaction the C-H bond that was originally part of the isopropyl group migrates to the secondary alkyl carbon. (See article – Rearrangements in Alkene Addition Reactions) See if you can draw a reasonable mechanism! Click to Flip These rearrangements can occur when a more stable carbocation can result from migration of a hydride or alkyl group. When a quaternary carbon is adjacent to a secondary carbocation, alkyl groups can migrate. Click to Flip Occasionally migrations between equivalently substituted groups can be favored, as in the example below. Click to Flip 7. Other Applications of Hydrohalogenation Alkynes will react with HX to give vinyl halides. A second equivalent of HX will give geminal dihalides. (For more, see Alkyne Hydrohalogenation) Dienes such as 1,3-butadiene will react with HX to give various products. See this article in the chapter on conjugated systems for more. (See article: 1,2- and 1,4-Addition of HX To Dienes) Aromatic rings such as benzene will not undergo addition reactions with HX. Aromatic rings tend to react through substitution. More in the chapter on aromatic rings. (See article: Introduction to Aromaticity) Carbocations are reactive intermediates and will readily combine with even poor Lewis bases. Sometimes those Lewis bases include other alkenes on the same molecule. This can result in cyclic molecules. For example, consider the reaction below: Click to Flip There are whole classes of molecules that are synthesized in nature via attack of alkenes on various carbocations.   One of the most prominent classes is terpenes. I don’t want to get into it in this article, but if you are looking for a good time, I strongly suggest looking at how the steroid skeleton of lanosterol is built up from the cyclization of squalene. [Note 5] This isn’t the cyclization of an alkene, but it’s another example of how rearrangements can occur in nature. In this example we start with alpha-pinene, one of the main ingredients in pine oil. Click to Flip 8. Summary HCl, HBr, and HI will all add to alkenes. The alkene acts as a nucleophile, forming a bond with the electrophilic proton of the acid. The reaction always occurs so as to form the most stable carbocation. This is responsible for the observations that led Markovnikov to postulate his rule in the first place. Be alert for the possibility of carbocation rearrangements when a more stable carbocation can be formed. This can sometimes even occur between carbons with similar substitution if it results in a resonance-stabilized carbocation. The reaction of HX with alkenes is essentially the same as the reaction of H3O+ with alkenes. They both follow what I call the Carbocation Pathway, one of the three key “buckets” of alkene reaction mechanisms that you might find helpful to remember. (See – Alkene Addition Reactions – The “Carbocation” Pathway) Notes Note 1. When peroxides (often written RO-OR) are present a very different reaction pathway occurs, where free-radical intermediates are involved. These reactions are anti-Markovnikov selective. For more on this reaction, see Free-Radical Addition of HBr To Alkenes. Note 2. Telling a small fib here, as this reaction does not always lack stereoselectivity. One particularly interesting set of results was in the addition of HBr to 1,2-dimethylcyclohexene in (the very non-polar solvent) pentane. It was found that addition occurred rapidly to give almost exclusively the trans product; letting it sit around for awhile led to some equilibration between stereoisomers. The authors propose that the reaction proceeds through a termolecular transition state (i.e. involving three molecules) with the alkene sandwiched between two molecules of HBr. Note 3. For our purposes, drawing the immediate formation of a carbocation is fine. Some studies look for the possibility of an even earlier intermediate called a “pi complex”, where H+ is coordinated to the pi-bond. As the bond between the pi-bond to the proton becomes stronger, the pi-complex then evolves into the carbocation intermediate. Note 4. Alkenes present a little bit of a dilemma in using curved arrows to describe the movement of electron pairs, since the double bond is not polarized and there is no obvious nucleophilic or electrophilic end. The convention in drawing arrows is that the carbon involved in bond formation is the one closest to the electrophile. For example here is an example of arrow-pushing that shows the right-hand carbon of the double bond forming a new bond to H: And here is an example of curved arrows showing formation of a new bond to the left side of the alkene: To solve this dilemma, various new conventions have been devised such as the bouncy arrow formalism and drawing a dashed line to indicate the bond being formed, although these have not exactly taken the world by storm. Note 5. If you are looking for a good time, this review outlines the whole rich and fascinating history of “cationic” alkene cyclizations, with a particular focus on how steroids and other related compounds are synthesized in nature. Quiz Yourself! Become a MOC member to see the clickable quiz with answers on the back.   Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. (Advanced) References and Further Reading Ingold’s “Structure and Mechanism in Organic Chemistry” is a valuable guide to the early literature on this topic. The Logic Behind Markovnikov’s Rule: Was It an Inspired Guess? ...No! D. E. Lewis, Angew. Chem. Int. Ed. 2021, 60, 4412. DOI: 10.1002/anie.202008228 Fun, accessible historical essay examining Markovnikov’s studies in the 1860’s-1870’s. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. Markownikoff, W. (1870) Justus Liebigs Ann. Chem., 153: 228-259. DOI: 10.1002/jlac.18701530204 The original Markovnikov paper. ELECTRON DISPLACEMENT IN CARBON COMPOUNDS I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS Howard J. Lucas and Archibald Y. Jameson Journal of the American Chemical Society 1924 46 (11), 2475-2482 DOI: 10.1021/ja01676a018 If not the earliest explanation of Markovnikov’s rule, certainly one of them. Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane Frank C. Whitmore and Franklin Johnston Journal of the American Chemical Society 1933 55 (12), 5020-5022 DOI: 10.1021/ja01339a053 One of the first clearly written out explanations of a carbocation rearrangement in addition of HX to alkenes. A subsequent paper (JACS 1950 1511) goes into more detail. The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene George S. Hammond and Thomas D. Nevitt Journal of the American Chemical Society 1954 76 (16), 4121-4123 DOI: 10.1021/ja01645a020 OK. When I wrote, above, that the addition of HX to alkenes is not stereoselective, I fibbed. The truth is that it can be stereoselective for anti addition if carried out at low temperatures in non polar solvents such as pentane. The proposed mechanism is not a free carbocation but a termolecular transition state involving two equivalents of H-Br. (Interestingly, though, the reaction of H3O+ with the same compound is not stereoselective). In the strongly polar solvent acetic acid, the reaction results predominantly (but not exclusively!) through the classic carbocation mechanism. Hydrochlorination of cyclohexene in acetic acid. Kinetic and product studies Robert C. Fahey, Michael W. Monahan, and C. Allen McPherson Journal of the American Chemical Society 1970 92 (9), 2810-2815 DOI: 10.1021/ja00712a034 Detailed kinetic studies of the addition of HCl to cyclohexene in acetic acid, discussing a possible third-order mechanism (rate = k[cyclohexene][HX]2). SPIROANNELATION OF ENOL SILANES: 2-OXO-5-METHOXYSPlRO[5.4]DECANE Lee, T. V.; Porter, J. R. Org. Synth. 1995, 72, 189 DOI: 10.15227/orgsyn.072.0189 The first reaction in the above procedure involves two steps – addition of HBr across the double bond and converting the aldehyde to a dimethyl acetal. Markovnikov’s Rule Robert C. Kerber Journal of Chemical Education 2007 84 (7), 1109 DOI: 10.1021/ed084p1109.1 A 2007 missive urging educators and textbook writers to retire the teaching of Markovnikov’s Rule. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids Ryan A. Yoder and Jeffrey N. Johnston Chemical Reviews 2005 105 (12), 4730-4756 DOI: 10.1021/cr040623l Last updated: March 5th, 2025 | Hydrohalogenation of Alkenes and Markovnikov’s Rule When hydrohalic acids (HCl, HBr, HI) are added to alkenes, addition reactions can occur, resulting in formation of a C-H and C-halogen bond and breakage of a C-C pi bond. The reaction tends to occur such that the halogen ends up attached to the carbon of the alkene attached to the fewest hydrogen atoms, a phenomenon known as Markovnikov’s Rule. Addition of H-X to alkenes occurs through a protonation of the alkene to give a carbocation intermediate, followed by addition of the halide to the carbocation. A better reformulation of Markovnikov’s rule is therefore that addition of HX to alkenes will proceed through the most stable carbocation, which is generally the more substituted carbon of the alkene. (Note that H-Br with peroxides (RO-OR) operates through a different reaction mechanism – see Free Radical Addition of H-Br to Alkenes). Carbocation rearrangements (hydride or alkyl shifts) can occur if they will result in a more stable carbocation intermediate. H-X will also add to alkynes (See: Addition of HX to alkynes) and dienes (See: 1,2- and 1,4- Addition of HX To Dienes) but will not add to aromatic rings. Table of Contents 1. Reaction of Alkenes With Hydrohalic Acids (HCl, HBr, HI) When alkenes are treated with hydrohalic acids (HCl, HBr, or HI) they form alkyl halides. This is sometimes called hydrohalogenation of alkenes since it results in the addition of hydrogen and a halogen. In these addition reactions: the C-C pi bond and the H-X bond breaks; a new C-H and C-X bond forms (where X is Cl, Br, or I). If we add up the bond dissociation energies (BDE’s) of the bonds that form (C-H, about 98 kcal/mol, and C-Cl, about 81 kcal/mol) and subtract their sum from those of the bonds that break (C-C pi, about 60 kcal/mol, and H-Cl, about 103 kcal/mol) the reaction is exothermic by about 18 kcal/mol for the addition of HCl. [Link to a useful table] Acid is required for these reactions to occur; no addition of halide to alkenes will happen in the absence of strong acid. (In other words, HCl = , but NaCl =). The new C-halogen bond tends to form on the most substituted carbon of the alkene (i.e. the one with the fewest carbons), and the new C-H bond tends to form on the carbon of the alkene containing the most hydrogens. 2. Markovnikov’s Rule: Regioselectivity of HX Addition to Alkenes The reactions of alkenes with has been known for over 150 years. When an alkene is not symmetrical, the reaction has the potential to form two different constitutional isomers (“regioisomers”). However, in many cases, one constitutional isomer is formed in a much higher proportion than the other. In other words, the reaction is regioselective. In an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens. This has come to be known as “Markovnikov’s Rule“. Markovnikov’s rule is what we would call an “empirical” rule. It was based purely on observed results, without any real underlying understanding of the mechanism of the reaction. In later years people had a hard time replicating Markovnikov’s results with HBr, often finding that the least substituted regioisomer was formed instead! Later on, in the 1930s the cause of this aberrant regioselectivity was found to be the presence of peroxides in solvent, which led to a free-radical process for addition of H-Br to alkenes, which does not occur with H-I or H-Cl. See article – Free-Radical addition of H-Br to Alkenes. [Note 1] Subsequently we tend to say, for better or worse, that addition reactions to alkenes that follow this pattern (such as their reaction with H3O+) are “Markovnikov-selective“, whereas reactions that follow the opposite pattern are “anti-Markovnikov selective” (such as hydroboration of alkenes). See if you can apply the pattern in the reaction of the alkene below (1-methylcyclopentene) with H-Cl. Click to Flip Another example is below. Draw the major product(s) and determine how they will be related: Click to Flip Can you work backwards to come up with the best starting material for this reaction? Click to Flip 3. Stereoselectivity (Or Lack Thereof) In Addition of HX To Alkenes When addition reactions occur across an alkene pi-bond, the (sp2-hybridized) trigonal planar carbons of the alkene are converted into (sp3-hybridized) tetrahedral carbons, and with this comes the potential for formation of stereoisomers. (See article: Types of Isomers) When the two new bonds to carbon are formed on the same face of the alkene, the addition is said to be “syn“ When the two new bonds are formed on opposite faces of the alkene, the addition is said to be “anti“. Addition reactions that give primarily syn or anti products are said to be stereoselective, and we will meet many examples in subsequent articles in this chapter (e.g.

halogenation is stereoselective for anti products, and hydroboration is stereoselective for syn products). Addition of H-X to alkenes gives a mixture of syn addition products and anti addition products [Note 2]. In other words, the reaction is not particularly stereoselective. This lack of stereoselectivity leads to mixtures of syn and anti addition products, in some cases each as mixtures of enantiomers. See if you can draw the products of the reaction below: Click to Flip 4. Hydrohalogenation of Alkenes: The Mechanism Markovnikov was one of the more prominent chemists of his era, but back in 1870 he didn't know why the reaction tended to give the more substituted product. The first to really figure it out was Lucas in 1924 [Ref], based on observations that alkyl groups are more "electron releasing". After many decades it was finally proposed that reaction goes through an intermediate carbocation. (The existence of carbocations was a fairly controversial subject until the 1930's). In the first step, the alkene (a nucleophile) is protonated by strong acid, resulting in a new carbocation. [Note 3] Depending on where protonation occurs, two different carbocations may be formed. Being electron-poor species, carbocations are stabilized by adjacent electron-donating groups as well as by delocalization through resonance. (See article – 3 Factors Which Stabilize Carbocations). The transition state leading to the most stable carbocation will be lower in energy, which tends to be the most substituted carbocation. The arrow pushing for alkenes reacting with acids like H-X can be a little ambiguous – see Note 4. So it is ultimately this carbocation intermediate which is the underlying reason for why Markovnikov's rule is observed. Carbocations have an empty p-orbital and readily accept a pair of electrons from whatever Lewis bases happen to be present in solution. In the second step, the best nucleophile present (which tends to be the halide ion) then attacks the carbocation, forming the alkyl halide. To reiterate: Markovnikov went to his grave not knowing this mechanism. Heck, many chemists of his time didn't even accept that carbon was tetrahedral! So if you didn't figure this mechanism out immediately, that's to be expected and certainly nothing to feel bad about. The body of knowledge that is chemistry is built up of thousands of little experiments that eventually grew into the framework we have today. 5. Reaction Energy Diagram For Alkene Hydrohalogenation Sometimes it can be helpful to trace out the energy profile of a reaction as it progresses from starting material to products. In these diagrams, peaks (local maxima) are transition states and valleys (local minima) are intermediates. A simple hydrohalogenation reaction has two steps – each of which has a transition state – and a single carbocation intermediate. In the first step, our intrepid alkene is protonated by strong acid, resulting in the high-energy transition state TS 1. This step has the highest activation energy (the barrier between reactants and transition state) making it the rate-determining step for this reaction. From the transition state (TS1) energy maximum, the reaction proceeds to the carbocation intermediate. The second step involves attack of the halide nucleophile on the carbocation, which proceeds through transition state 2 (TS2). Note that the activation energy for this step is considerably less than for protonation of the alkene – in other words, it will be the fast step. The reaction then proceeds through TS2 to give the final product, the alkyl halide. 6. Carbocation Rearrangements – Hydride and Alkyl Shifts One key to the proposal of a carbocation intermediate was the observation that some hydrohalogenation reactions give products of carbocation rearrangements in addition to the expected addition product. For example when 4-methyl-1-butene was treated with HCl and allowed to sit at room temperature for an extended period, the product mixture was found to contain about half the expected Markovnikov addition product in addition to a new tertiary alkyl halide. [Ref] In this reaction the C-H bond that was originally part of the isopropyl group migrates to the secondary alkyl carbon. (See article – Rearrangements in Alkene Addition Reactions) See if you can draw a reasonable mechanism! Click to Flip These rearrangements can occur when a more stable carbocation can result from migration of a hydride or alkyl group. When a quaternary carbon is adjacent to a secondary carbocation, alkyl groups can migrate. Click to Flip Occasionally migrations between equivalently substituted groups can be favored, as in the example below. Click to Flip 7. Other Applications of Hydrohalogenation Alkynes will react with HX to give vinyl halides. A second equivalent of HX will give geminal dihalides. (For more, see Alkyne Hydrohalogenation) Dienes such as 1,3-butadiene will react with HX to give various products. See this article in the chapter on conjugated systems for more. (See article: 1,2- and 1,4-Addition of HX To Dienes) Aromatic rings such as benzene will not undergo addition reactions with HX. Aromatic rings tend to react through substitution. More in the chapter on aromatic rings. (See article: Introduction to Aromaticity) Carbocations are reactive intermediates and will readily combine with even poor Lewis bases. Sometimes those Lewis bases include other alkenes on the same molecule. This can result in cyclic molecules. For example, consider the reaction below: Click to Flip There are whole classes of molecules that are synthesized in nature via attack of alkenes on various carbocations. One of the most prominent classes is terpenes. I don't want to get into it in this article, but if you are looking for a good time, I strongly suggest looking at how the steroid skeleton of lanosterol is built up from the cyclization of squalene. [Note 5] This isn't the cyclization of an alkene, but it's another example of how rearrangements can occur in nature. In this example we start with alpha-pinene, one of the main ingredients in pine oil. Click to Flip 8. Summary HCl, HBr, and HI will all add to alkenes. The alkene acts as a nucleophile, forming a bond with the electrophilic proton of the acid. The reaction always occurs so as to form the most stable carbocation. This is responsible for the observations that led Markovnikov to postulate his rule in the first place. Be alert for the possibility of carbocation rearrangements when a more stable carbocation can be formed. This can sometimes even occur between carbons with similar substitution if it results in a resonance-stabilized carbocation. The reaction of HX with alkenes is essentially the same as the reaction of H3O+ with alkenes. They both follow what I call the Carbocation Pathway, one of the three key "buckets" of alkene reaction mechanisms that you might find helpful to remember. (See – Alkene Addition Reactions – The "Carbocation" Pathway) Notes Note 1. When peroxides (often written RO-OR) are present a very different reaction pathway occurs, where free-radical intermediates are involved. These reactions are anti-Markovnikov selective. For more on this reaction, see Free-Radical Addition of HBr To Alkenes. Note 2. Telling a small fib here, as this reaction does not always lack stereoselectivity. One particularly interesting set of results was in the addition of HBr to 1,2-dimethylcyclohexene in (the very non-polar solvent) pentane. It was found that addition occurred rapidly to give almost exclusively the trans product; letting it sit around for awhile led to some equilibration between stereoisomers. The authors propose that the reaction proceeds through a termolecular transition state (i.e. involving three molecules) with the alkene sandwiched between two molecules of HBr. Note 3. For our purposes, drawing the immediate formation of a carbocation is fine. Some studies look for the possibility of an even earlier intermediate called a "pi complex", where H+ is coordinated to the pi-bond. As the bond between the pi-bond to the proton becomes stronger, the pi-complex then evolves into the carbocation intermediate. Note 4. Alkenes present a little bit of a dilemma in using curved arrows to describe the movement of electron pairs, since the double bond is not polarized and there is no obvious nucleophilic or electrophilic end. The convention in drawing arrows is that the carbon involved in bond formation is the one closest to the electrophile. For example here is an example of arrow-pushing that shows the right-hand carbon of the double bond forming a new bond to H: And here is an example of curved arrows showing formation of a new bond to the left side of the alkene: To solve this dilemma, various new conventions have been devised such as the bouncy arrow formalism and drawing a dashed line to indicate the bond being formed, although these have not exactly taken the world by storm. Note 5. If you are looking for a good time, this review outlines the whole rich and fascinating history of "cationic" alkene cyclizations, with a particular focus on how steroids and other related compounds are synthesized in nature. Quiz Yourself! Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. (Advanced) References and Further Reading Ingold's "Structure and Mechanism in Organic Chemistry" is a valuable guide to the early literature on this topic. The Logic Behind Markovnikov's Rule: Was It an Inspired Guess? ...No! D. E. Lewis, Angew. Chem. Int. Ed. 2021, 60, 4412. DOI: 10.1002/anie.202008228 Fun, accessible historical essay examining Markovnikov's studies in the 1860's-1870's. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. Markownikoff, W. (1870) Justus Liebigs Ann. Chem., 153: 228-259. DOI: 10.1002/jlac.18701530204 The original Markovnikov paper. ELECTRON DISPLACEMENT IN CARBON COMPOUNDS I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS Howard J. Lucas and Archibald Y. Jameson Journal of the American Chemical Society 1924 46 (11), 2475-2482 DOI: 10.1021/ja01676a018 If not the earliest explanation of Markovnikov's rule, certainly one of them. Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane Frank C. Whitmore and Franklin Johnston Journal of the American Chemical Society 1933 55 (12), 5020-5022 DOI: 10.1021/ja01339a053 One of the first clearly written out explanations of a carbocation rearrangement in addition of HX to alkenes. A subsequent paper (JACS 1950 1511) goes into more detail. The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene George S. Hammond and Thomas D. Nevitt Journal of the American Chemical Society 1954 76 (16), 4121-4123 DOI: 10.1021/ja01645a020 OK. When I wrote, above, that the addition of HX to alkenes is not stereoselective, I fibbed. The truth is that it can be stereoselective for anti addition if carried out at low temperatures in non polar solvents such as pentane. The proposed mechanism is not a free carbocation but a termolecular transition state involving two equivalents of H-Br. (Interestingly, though, the reaction of H3O+ with the same compound is not stereoselective). In the strongly polar solvent acetic acid, the reaction results predominantly (but not exclusively!) through the classic carbocation mechanism. Hydrochlorination of cyclohexene in acetic acid. Kinetic and product studies Robert C. Fahey, Michael W. Monahan, and C. Allen McPherson Journal of the American Chemical Society 1970 92 (9), 2810-2815 DOI: 10.1021/ja00712a034 Detailed kinetic studies of the addition of HCl to cyclohexene in acetic acid, discussing a possible third-order mechanism (rate = k[cyclohexene][HX]2). SPIROANNELATION OF ENOL SILANES: 2-OXO-5-METHOXYSPIRO[5.4]DECANE Lee, T. V.; Porter, J. R. Org. Synth. 1995, 72, 189 DOI: 10.15227/orgsyn.072.0189 The first reaction in the above procedure involves two steps – addition of HBr across the double bond and converting the aldehyde to a dimethyl acetal. Markovnikov's Rule Robert C. Kerber Journal of Chemical Education 2007 84 (7), 1109 DOI: 10.1021/ed084p1109.1 A 2007 missive urging educators and textbook writers to retire the teaching of Markovnikov's Rule. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids Ryan A. Yoder and Jeffrey N. Johnston Chemical Reviews 2005 105 (12), 4730-4756 DOI: 10.1021/cr040623l Hydrohalogenation is a type of electrophilic addition reaction that occurs in unsaturated compounds like alkene and alkyne. A hydrogen halide (HX), such as hydrogen chloride (HCl) or hydrogen bromide (HBr), adds to an alkene, producing the corresponding haloalkanes or alkyl halides. The reaction is carefully carried out in the presence of a non-polar or inert solvent like carbon tetrachloride (CCl4). The pi bonds in alkenes and alkynes are easily susceptible to electrophilic attack. General Reaction To understand the fundamental reaction of hydrohalogenation, let us take an alkene R1HC=CH2, which reacts with a hydrogen halide HX (X = Cl, Br, F, I). The reaction yields two alkyl halides – R1HXC-CH3 as the major product and R1H2C-CH2X as the minor product. The reaction is as follows: R1HC=CH2 + HX → R1HXC-CH3 (major) + R1H2C-CH2X (minor) Hydrohalogenation 1. Reaction of Ethene (CH2=CH2) with HBr Ethene is a symmetrical alkene containing two carbon atoms. It reacts with HBr in the presence of CCl4, producing bromoethane or ethyl bromide (CH3CH2Br). CH2=CH2 + HBr → CH3CH2Br Hydrohalogenation of Alkenes 2. Reaction of Propene (CH3CH=CH2) with HCl Propene is an unsaturated alkene consisting of a three-carbon chain with two carbon atoms on either side of the double bond. When it reacts with hydrogen chloride, propene produces 2-chloropropane or 2-propyl chloride (CH3CHClCH3) as the major product and 1-chloropropane (CH3CH2CH2Cl) as the minor product. CH3CH=CH2 + HCl → CH3CHClCH3 (major product, more stable) + CH3CH2CH2Cl (minor product, less stable) Here, CH3CHClCH3 and CH3CH2CH2Cl are constitutional isomers of each other. The fundamental mechanism of hydrohalogenation of alkenes is as follows: First, the nucleophilic pi bond of the alkene breaks down as it tries to grab the electrophilic H+ from HX.Then, Markovnikov's rule is applied. H+ adds to the less substituted carbon atom. The more substituted carbon is now deficient in electrons, thus turning into a carbocation.Finally, the halide ion (X–) present in the solution attacks the carbocation forming a haloalkane or alkyl halide. To understand the mechanism of hydrohalogenation of alkenes in-depth, let us go through each step in detail: Step 1: Use an Inert Solvent An inert or non-polar solvent, such as dichloromethane (CH2Cl2) and carbon tetrachloride (CCl4), dissolves the reactants and reagents. However, it does not interfere in the reaction process. If any non-inert or polar solvent is used for the reaction, the result will be completely different. For instance, if carried out in water, the final product will be alcohol. On the other hand, if carried out in an alcoholic medium, the product will be ether. Step 2: Understand the Nature of the Molecules Now, try to understand the nature of the reacting molecules. Here, the reactants are an alkene and a hydrogen halide (HX). HX molecules are highly polar since halogens like Cl, Br, I, and F are highly electronegative. Due to this, the halogen becomes partially negative (δ–). It pulls the electrons away from hydrogen, making it partially positive (δ+). So, hydrogen halide provides both an electrophile (H+) and a nucleophile (X–). [Note – HF seldom shows this reaction due to fluorine's high electronegativity and poor reactivity.] Step 3: Break the Pi(π) Bond In this step, the alkene's pi (π) bond reaches out to grab the electrophilic hydrogen atom. For this, a pi (π) electron must let go of the carbon atom that it is bound to, yielding a carbocation. The carbocation is a high-energy intermediate, making this the reaction's rate-determining step (slow step). Markovnikov's Rule and Regioselectivity The next thing that comes to our mind is, which carbon atom of the double bond will take up the hydrogen? According to Markovnikov's rule, the carbon with fewer substitutions in a double bond of an unsymmetrical alkene will first grab the H+, producing a carbocation. In other words, the carbon with more hydrogen atoms attached to it will take the H+. So, the more substituted carbon atom of the double bond is converted to a stable carbocation, an electrophile. It means that the reaction is regioselective. Rearrangement of Carbocation Generally, the formation of carbocation follows Markovnikov's rule. However, there is a chance that the carbocation rearranges by shifting the hydride (H–) or methyl (CH3–) group and result in more than one stable carbocation. The stability of carbocation is as follows: 3° > 2° > 1°. The reaction will always prefer the 2° or 3° carbocation as it is more stable than 1°. So, Markovnikov's rule does not hold for every case, as it does not deal with carbocation rearrangement. Example of Carbocation Rearrangement When 3-methyl-1-butene (CH3CH(CH3)CH=CH2) reacts with hydrogen bromide (HBr), the major product will be 3-methyl-2-bromobutane CH3CH(CH3)CH(Br)-CH3. CH3CH(CH3)CH=CH2 + HBr → CH3CH(CH3)CH(Br)-CH3 However, there is a probability of producing 3° carbocation by 1,2-hydride shifting. As we know that 3° carbocation is more stable than 2°, this rearrangement will produce a more stable alkyl halide. Step 1: Formation of 2° carbocation CH3CH(CH3)CH=CH2 + HBr → CH3CH(CH3)C+HCH3 Step 2: Rearrangement by 1,2-hydride shift to form 3° carbocation CH3CH(CH3)C+HCH3 → CH3C+(CH3)CH2-CH3 Step 3: Addition of bromide (Br–) CH3C+(CH3)CH2-CH3 + Br– → CH3CBr(CH3)CH2-CH3 Anti-Markovnikov's Rule Sometimes, H+ may bind to a more substituted carbon rather than the least substituted carbon, following anti-Markovnikov's rule. This process is quite unusual, as carbocations formed in the majority during hydrohalogenation reactions tend to favor the more substituted carbon. Step 4: Attack of the Halide In this step, the nucleophilic halide ion (X–) attacks the electrophilic carbocation. The halogen uses one of its lone electron pairs to attack the carbocation forming a sigma bond. In this context, stereochemistry is essential in determining the final product. Stereochemistry The nucleophile may attack the carbocation from either direction – top or bottom of the pi-bond. So, a mixture of syn (adding the substitutes to the same side of the pi-bond) and anti-products (adding the substitutes to the opposite sides of the pi-bond) can be expected here. Hydrohalogenation Mechanism Like alkenes, alkynes also undergo hydrohalogenation reactions. Upon adding HX, alkynes produce a vinyl halide. This alkene is later converted into a geminal dihalide upon the second electrophilic addition of HX. Like alkenes, the process starts by adding H+ to the π bond, forming a vinyl carbocation. The reaction is performed in the dark in a peroxide-free solvent. The more stable 2° carbocation is then attacked by the halide ion (X–), forming vinyl halide. The resulting haloalkene is less reactive since the electronegative halogen decreases the electron density of the double bond by the inductive effect, i.e., pulling the negative charge of the double bond towards itself. The reaction can be stopped at this point. If further HX is added, another halide ion (X–) gets attached to the same carbocation, yielding germinal dihalide. It is an organic compound containing two halide groups attached to the same carbon atom. General Reactions Step 1: Formation of 2° Vinyl Carbocation RC≡CH + HX → RC+=CH2 Step 2: Formation of vinyl halide RC+=CH2 + X– → RCX=CH2 Step 3: Formation of 2° Carbocation RC(X)=CH2 + HX → RC+(X)-CH3 Step 4: Formation of Geminal Dihalide RC+(X)-CH3+ Cl– → RC(X)(X)-CH3 Example Consider the reaction of propyne (CH3-C ≡C-H) with hydrogen bromide (HBr). Step 1: Formation of 2° vinyl carbocation CH3-C ≡C-H + HBr → CH3C+=CH2 Step 2: Formation of 2-bromopropene CH3C+=CH2 + Br– → CH3CBr=CH2 Step 3: Formation of 2° carbocation CH3CBr=CH2 + HBr → CH3C+Br-CH3 Step 4: Formation of 2,2-dibromopropane CH3C+Br-CH3 + Br– → CH3C(Br)(Br)-CH3 Hydrohalogenation of Alkynes P.1. Mention the major product formed for the following reaction: Addition of HCl to 3,3-dimethyl-1-butene. Sol. Following Markovnikov's rule, 3,3-dimethyl-1-butene (CH3-C(CH3)(CH3)CH=CH2) first forms a 2° carbocation, which later gets attacked by Cl– to form 3,3 dimethyl-2-bromobutane (CH3-C(CH3)(CH3)CHBr-CH3). The reaction is as follows: CH3-C(CH3)(CH3)CH=CH2 + HBr → CH3-C(CH3)(CH3)C+H-CH3 → CH3-C(CH3)(CH3)CHBr-CH3 There is also a possibility to produce a 3° carbocation by shifting the adjacent methyl group. Step 1: CH3-C(CH3)(CH3)CH=CH2 + HBr → CH3C+CH3-CHCH3(CH3) + Br– Step 2: CH3C+CH3-CH(CH3)(CH3) + Br– → CH3CBrCH3-CHCH3(CH3) As 3° carbocation is more stable than 2° carbocation, the second mechanism will be preferred. P.2. What happens when acetylene is treated with HBr? Sol. When acetylene (CH≡CH) is treated with HBr, it forms ethylidene bromide (CH3CHBr2). The reaction is as follows: Step 1: HC≡CH + HBr → H2C=C+H + Br– → CH2=CHBr Step 2: H2C=CHBr + HBr → H3C-C+HBr + Br– → H3C-CHBr2 References Last updated: March 5th, 2025 | Hydrohalogenation of Alkenes and Markovnikov's Rule When hydrohalic acids (HCl, HBr, HI) are added to alkenes, addition reactions can occur, resulting in formation of a C-H and C-halogen bond and breakage of a C-C pi bond. The reaction tends to occur such that the halogen ends up attached to the carbon of the alkene attached to the fewest hydrogen atoms, a phenomenon known as Markovnikov's Rule. Addition of H-X to alkenes occurs through a protonation of the alkene to give a carbocation intermediate, followed by addition of the halide to the carbocation. A better reformulation of Markovnikov's rule is therefore that addition of HX to alkenes will proceed through the most stable carbocation, which is generally the more substituted carbon of the alkene. (Note that H-Br with peroxides (RO-OR) operates through a different reaction mechanism – see Free Radical Addition of H-Br to Alkenes). Carbocation rearrangements (hydride or alkyl shifts) can occur if they will result in a more stable carbocation intermediate. H-X will also add to alkynes (See: Addition of HX to alkynes) and dienes (See: 1,2- and 1,4- Addition of HX To Dienes) but will not add to aromatic rings. Table of Contents 1. Reaction of Alkenes With Hydrohalic Acids (HCl, HBr, HI) When alkenes are treated with hydrohalic acids (HCl, HBr, or HI) they form alkyl halides. This is sometimes called hydrohalogenation of alkenes since it results in the addition of hydrogen and a halogen. In these addition reactions: the C-C pi bond and the H-X bond breaks; a new C-H and C-X bond forms (where X is Cl, Br, or I). If we add up the bond dissociation energies (BDE's) of the bonds that form (C-H, about 98 kcal/mol, and C-Cl, about 81 kcal/mol) and subtract their sum from those of the bonds that break (C-C pi, about 60 kcal/mol, and H-Cl, about 103 kcal/mol) the reaction is exothermic by about 18 kcal/mol for the addition of HCl. [Link to a useful table] Acid is required for these reactions to occur; no addition of halide to alkenes will happen in the absence of strong acid. (In other words, HCl = , but NaCl =). The new C-halogen bond tends to form on the most substituted carbon of the alkene (i.e. the one with the fewest carbons), and the new C-H bond tends to form on the carbon of the alkene containing the most hydrogens. 2. Markovnikov's Rule: Regioselectivity of HX Addition to Alkenes The reactions of alkenes with has been known for over 150 years. When an alkene is not symmetrical, the reaction has the potential to form two different constitutional isomers ("regioisomers"). However, in many cases, one constitutional isomer is formed in a much higher proportion than the other. In other words, the reaction is regioselective. In an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens. This has come to be known as "Markovnikov's Rule". Markovnikov's rule is what we would call an "empirical" rule. It was based purely on observed results, without any real underlying understanding of the mechanism of the reaction. In later years people had a hard time replicating Markovnikov's results with HBr, often finding that the least substituted regioisomer was formed instead! Later on, in the 1930s the cause of this aberrant regioselectivity was found to be the presence of peroxides in solvent, which led to a free-radical process for addition of H-Br to alkenes, which does not occur with H-I or H-Cl. See article – Free-Radical addition of H-Br to Alkenes. [Note 1] Subsequently we tend to say, for better or worse, that addition reactions to alkenes that follow this pattern (such as their reaction with H3O+) are "Markovnikov-selective", whereas reactions that follow the opposite pattern are "anti-Markovnikov selective" (such as hydroboration of alkenes). See if you can apply the pattern in the reaction of the alkene below (1-methylcyclopentene) with H-Cl. Click to Flip Another example is below. Draw the major product(s) and determine how they will be related: Click to Flip Can you work backwards to come up with the best starting material for this reaction? Click to Flip 3. Stereoselectivity (Or Lack Thereof) In Addition of HX To Alkenes When addition reactions occur across an alkene pi-bond, the (sp2-hybridized) trigonal planar carbons of the alkene are converted into (sp3-hybridized) tetrahedral carbons, and with this comes the potential for formation of stereoisomers. (See article: Types of Isomers) When the two new bonds to carbon are formed on the same face of the alkene, the addition is said to be "syn" When the two new bonds are formed on opposite faces of the alkene, the addition is said to be "anti". Addition reactions that give primarily syn or anti products are said to be stereoselective, and we will meet many examples in subsequent articles in this chapter (e.g. halogenation is stereoselective for anti products, and hydroboration is stereoselective for syn products). Addition of H-X to alkenes gives a mixture of syn addition products and anti addition products [Note 2]. In other words, the reaction is not particularly stereoselective. This lack of stereoselectivity leads to mixtures of syn and anti addition products, in some cases each as mixtures of enantiomers. See if you can draw the products of the reaction below: Click to Flip 4. Hydrohalogenation of Alkenes: The Mechanism Markovnikov was one of the more prominent chemists of his era, but back in 1870 he didn't know why the reaction tended to give the more substituted product. The first to really figure it out was Lucas in 1924 [Ref], based on observations that alkyl groups are more "electron releasing". After many decades it was finally proposed that reaction goes through an intermediate carbocation. (The existence of carbocations was a fairly controversial subject until the 1930's). In the first step, the alkene (a nucleophile) is protonated by strong acid, resulting in a new carbocation. [Note 3] Depending on where protonation occurs, two different carbocations may be formed. Being electron-poor species, carbocations are stabilized by adjacent electron-donating groups as well as by delocalization through resonance. (See article – 3 Factors Which Stabilize Carbocations). The transition state leading to the most stable carbocation will be lower in energy, which tends to be the most substituted carbocation. The arrow pushing for alkenes reacting with acids like H-X can be a little ambiguous – see Note 4. So it is ultimately this carbocation intermediate which is the underlying reason for why Markovnikov's rule is observed. Carbocations have an empty p-orbital and readily accept a pair of electrons from whatever Lewis bases happen to be present in solution. In the second step, the best nucleophile present (which tends to be the halide ion) then attacks the carbocation, forming the alkyl halide. To reiterate: Markovnikov went to his grave not knowing this mechanism. Heck, many chemists of his time didn't even accept that carbon was tetrahedral! So if you didn't figure this mechanism out immediately, that's to be expected and certainly nothing to feel bad about. The body of knowledge that is chemistry is built up of thousands of little experiments that eventually grew into the framework we have today. 5. Reaction Energy Diagram For Alkene Hydrohalogenation Sometimes it can be helpful to trace out the energy profile of a reaction as it progresses from starting material to products. In these diagrams, peaks (local maxima) are transition states and valleys (local minima) are intermediates. A simple hydrohalogenation reaction has two steps – each of which has a transition state – and a single carbocation intermediate. In the first step, our intrepid alkene is protonated by strong acid, resulting in the high-energy transition state TS 1. This step has the highest activation energy (the barrier between reactants and transition state) making it the rate-determining step for this reaction. From the transition state (TS1) energy maximum, the reaction proceeds to the carbocation intermediate. The second step involves attack of the halide nucleophile on the carbocation, which proceeds through transition state 2 (TS2). Note that the activation energy for this step is considerably less than for protonation of the alkene – in other words, it will be the fast step. The reaction then proceeds through TS2 to give the final product, the alkyl halide. 6. Carbocation Rearrangements – Hydride and Alkyl Shifts One key to the proposal of a carbocation intermediate was the observation that some hydrohalogenation reactions give products of carbocation rearrangements in addition to the expected addition product. For example when 4-methyl-1-butene was treated with HCl and allowed to sit at room temperature for an extended period, the product mixture was found to contain about half the expected Markovnikov addition product in addition to a new tertiary alkyl halide. [Ref] In this reaction the C-H bond that was originally part of the isopropyl group migrates to the secondary alkyl carbon. (See article – Rearrangements in Alkene Addition Reactions) See if you can draw a reasonable mechanism! Click to Flip These rearrangements can occur when a more stable carbocation can result from migration of a hydride or alkyl group. When a quaternary carbon is adjacent to a secondary carbocation, alkyl groups can migrate. Click to Flip Occasionally migrations between equivalently substituted groups can be favored, as in the example below. Click to Flip 7. Other Applications of Hydrohalogenation Alkynes will react with HX to give vinyl halides. A second equivalent of HX will give geminal dihalides. (For more, see Alkyne Hydrohalogenation) Dienes such as 1,3-butadiene will react with HX to give various products. See this article in the chapter on conjugated systems for more. (See article: 1,2- and 1,4-Addition of HX To Dienes) Aromatic rings such as benzene will not undergo addition reactions with HX. Aromatic rings tend to react through substitution. More in the chapter on aromatic rings. (See article: Introduction to Aromaticity) Carbocations are reactive intermediates and will readily combine with even poor Lewis bases. Sometimes those Lewis bases include other alkenes on the same molecule. This can result in cyclic molecules. For example, consider the reaction below: Click to Flip There are whole classes of molecules that are synthesized in nature via attack of alkenes on various carbocations. One of the most prominent classes is terpenes. I don't want to get into it in this article, but if you are looking for a good time, I strongly suggest looking at how the steroid skeleton of lanosterol is built up from the cyclization of squalene. [Note 5] This isn't the cyclization of an alkene, but it's another example of how rearrangements can occur in nature. In this example we start with alpha-pinene, one of the main ingredients in pine oil. Click to Flip 8. Summary HCl, HBr, and HI will all add to alkenes. The alkene acts as a nucleophile, forming a bond with the electrophilic proton of the acid. The reaction always occurs so as to form the most stable carbocation. This is responsible for the observations that led Markovnikov to postulate his rule in the first place. Be alert for the possibility of carbocation rearrangements when a more stable carbocation can be formed. This can sometimes even occur between carbons with similar substitution if it results in a resonance-stabilized carbocation. The reaction of HX with alkenes is essentially the same as the reaction of H3O+ with alkenes. They both follow what I call the Carbocation Pathway, one of the three key "buckets" of alkene reaction mechanisms that you might find helpful to remember. (See – Alkene Addition Reactions – The "Carbocation" Pathway) Notes Note 1. When peroxides (often written RO-OR) are present a very different reaction pathway occurs, where free-radical intermediates are involved. These reactions are anti-Markovnikov selective. For more on this reaction, see Free-Radical Addition of HBr To Alkenes. Note 2. Telling a small fib here, as this reaction does not always lack stereoselectivity. One particularly interesting set of results was in the addition of HBr to 1,2-dimethylcyclohexene in (the very non-polar solvent) pentane. It was found that addition occurred rapidly to give almost exclusively the trans product; letting it sit around for awhile led to some equilibration between stereoisomers. The authors propose that the reaction proceeds through a termolecular transition state (i.e. involving three molecules) with the alkene sandwiched between two molecules of HBr. Note 3. For our purposes, drawing the immediate formation of a carbocation is fine. Some studies look for the possibility of an even earlier intermediate called a "pi complex", where H+ is coordinated to the pi-bond. As the bond between the pi-bond to the proton becomes stronger, the pi-complex then evolves into the carbocation intermediate. Note 4. Alkenes present a little bit of a dilemma in using curved arrows to describe the movement of electron pairs, since the double bond is not polarized and there is no obvious nucleophilic or electrophilic end. The convention in drawing arrows is that the carbon involved in bond formation is the one closest to the electrophile. For example here is an example of arrow-pushing that shows the right-hand carbon of the double bond forming a new bond to H: And here is an example of curved arrows showing formation of a new bond to the left side of the alkene: To solve this dilemma, various new conventions have been devised such as the bouncy arrow formalism and drawing a dashed line to indicate the bond being formed, although these have not exactly taken the world by storm. Note 5. If you are looking for a good time, this review outlines the whole rich and fascinating history of "cationic" alkene cyclizations, with a particular focus on how steroids and other related compounds are synthesized in nature. Quiz Yourself! Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. (Advanced) References and Further Reading Ingold's "Structure and Mechanism in Organic Chemistry" is a valuable guide to the early literature on this topic. The Logic Behind Markovnikov's Rule: Was It an Inspired Guess? ...No! D. E. Lewis, Angew. Chem. Int. Ed. 2021, 60, 4412. DOI: 10.1002/anie.202008228 Fun, accessible historical essay examining Markovnikov's studies in the 1860's-1870's. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. Markownikoff, W. (1870) Justus Liebigs Ann. Chem., 153: 228-259. DOI: 10.1002/jlac.18701530204 The original Markovnikov paper. ELECTRON DISPLACEMENT IN CARBON COMPOUNDS I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS Howard J. Lucas and Archibald Y. Jameson Journal of the American Chemical Society 1924 46 (11), 2475-2482 DOI: 10.1021/ja01676a018 If not the earliest explanation of Markovnikov's rule, certainly one of them. Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane Frank C. Whitmore and Franklin Johnston Journal of the American Chemical Society 1933 55 (12), 5020-5022 DOI: 10.1021/ja01339a053 One of the first clearly written out explanations of a carbocation rearrangement in addition of HX to alkenes. A subsequent paper (JACS 1950 1511) goes into more detail. The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene George S. Hammond and Thomas D. Nevitt Journal of the American Chemical Society 1954 76 (16), 4121-4123 DOI: 10.1021/ja01645a020 OK. When I wrote, above, that the addition of HX to alkenes is not stereoselective, I fibbed. The truth is that it can be stereoselective for anti addition if carried out at low temperatures in non polar solvents such as pentane. The proposed mechanism is not a free carbocation but a termolecular transition state involving two equivalents of H-Br. (Interestingly, though, the reaction of H3O+ with the same compound is not stereoselective). In the strongly polar solvent acetic acid, the reaction results predominantly (but not exclusively!) through the classic carbocation mechanism. Hydrochlorination of cyclohexene in acetic acid. Kinetic and product studies Robert C. Fahey, Michael W. Monahan, and C. Allen McPherson Journal of the American Chemical Society 1970 92 (9), 2810-2815 DOI: 10.1021/ja00712a034 Detailed kinetic studies of the addition of HCl to cyclohexene in acetic acid, discussing a possible third-order mechanism (rate = k[cyclohexene][HX]2). SPIROANNELATION OF ENOL SILANES: 2-OXO-5-METHOXYSPIRO[5.4]DECANE Lee, T. V.; Porter, J. R. Org. Synth. 1995, 72, 189 DOI: 10.15227/orgsyn.072.0189 The first reaction in the above procedure involves two steps – addition of HBr across the double bond and converting the aldehyde to a dimethyl acetal. Markovnikov's Rule Robert C. Kerber Journal of Chemical Education 2007 84 (7), 1109 DOI: 10.1021/ed084p1109.1 A 2007 missive urging educators and textbook writers to retire the teaching of Markovnikov's Rule. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids Ryan A. Yoder and Jeffrey N. Johnston Chemical Reviews 2005 105 (12), 4730-4756 DOI: 10.1021/cr040623l Tutorial on the alkene hydrohalogenation reaction, which converts alkenes to alkyl halides using hydrogen halides. The alkene hydrohalogenation reaction is an electrophilic addition reaction which converts alkenes into alkyl halides. The alkene reacts with a hydrogen halide (HX, where X is Cl, Br, or I), breaking the alkene π bond, adding a hydrogen to one alkene carbon, and adding a halogen atom (Cl, Br, or I) to the other. The position where the halogen is added can be predicted by Markovnikov's rule. This rule states that, in an electrophilic addition reaction, the nucleophile (here, the halogen) will be added to the more highly substituted alkene carbon (the alkene carbon that has more alkyl groups) to give the Markovnikov product. The mechanism of alkene hydrohalogenation is very similar to other electrophilic addition reactions, especially the alkene hydration reaction. Let's go through the mechanism of this reaction, where an alkene reacts with hydrogen bromide (HBr) to produce an alkyl halide: Like other electrophilic addition reactions, this mechanism begins with the nucleophilic attack of the alkene π electrons (i.e., the double bond) onto an electrophile. Here, the electrophile is the hydrogen atom of HBr, which carries a partial positive charge. Draw an arrow from the alkene double bond to the hydrogen atom of hydrogen bromide. This leads to the cleavage of the H-Br bond, as shown with an arrow going from the H-Br bond to the bromine. This results in a negatively charged bromide ion. The hydrogen from HBr is added to one of the alkene carbons, while the other alkene carbon gets a positive charge. The position that becomes positively charged is determined based on carbocation stability. If the carbon on the right is protonated, a tertiary carbocation is formed (top arrow), and if the carbon of the left is protonated, a primary carbocation is formed (bottom arrow): As carbocations with more substituents are more stable, the top reaction arrow is much more favourable, and so the tertiary carbocation is the major product of the first step. Now that the carbocation formed, the second step is the nucleophilic attack of the bromide ion onto the electrophilic carbocation, forming the alkyl halide product. This is shown by drawing an arrow from the bromide ion to the carbocation carbon: Markovnikov's rule, which predicts that the nucleophile in an electrophilic addition reaction will add to the more highly substituted alkene carbon, is based on carbocation stability. In these reactions, formation of the more substituted (and thus more stable) carbocation intermediate is preferred. As the more substituted carbocation is preferentially formed, the nucleophile will add to this carbocation, and so the nucleophile is added to the more substituted carbon. In the alkene hydrohalogenation reaction, two different products are possible, depending on which alkene carbon the halogen atom is added to. These two products are regioisomers, which are structural isomers that differ based on the position of a substituent or functional group (in this case, the halogen atom). As this reaction follows Markovnikov's rule, one regioisomer is usually the major product – thus, this reaction is said to be regioselective, and the Markovnikov product regioisomer is preferentially formed. For other alkenes, in which both alkene carbons have the same number of substituents, this reaction may be less regioselective, and can give a mixture of products. Note that some alkene reactions, such as the hydroboration-oxidation reaction, preferentially form the anti-Markovnikov product, in which the nucleophile ultimately ends up on the less substituted alkene carbon. The alkene hydrohalogenation reaction converts an alkene into an alkyl halide, using a hydrogen halide. This is an electrophilic addition reaction where the alkene nucleophilically attacks an electrophile, a carbocation is formed, and a second nucleophile attacks the carbocation. This reaction follows the Markovnikov's rule, as the carbocation is preferentially formed on the more highly substituted alkene carbon. This is thus a regioselective reaction, as one regioisomer is usually the major product (the Markovnikov product). Alkene Hydration Reaction – a related electrophilic addition reaction, which converts alkenes into alcohols. Last updated: March 5th, 2025 | Hydrohalogenation of Alkenes and Markovnikov's Rule When hydrohalic acids (HCl, HBr, HI) are added to alkenes, addition reactions can occur, resulting in formation of a C-H and C-halogen bond and breakage of a C-C pi bond. The reaction tends to occur such that the halogen ends up attached to the carbon of the alkene attached to the fewest hydrogen atoms, a phenomenon known as Markovnikov's Rule. Addition of H-X to alkenes occurs through a protonation of the alkene to give a carbocation intermediate, followed by addition of the halide to the carbocation. A better reformulation of Markovnikov's rule is therefore that addition of HX to alkenes will proceed through the most stable carbocation, which is generally the more substituted carbon of the alkene. (Note that H-Br with peroxides (RO-OR) operates through a different reaction mechanism – see Free Radical Addition of H-Br to Alkenes). Carbocation rearrangements (hydride or alkyl shifts) can occur if they will result in a more stable carbocation intermediate. H-X will also add to alkynes (See: Addition of HX to alkynes) and dienes (See: 1,2- and 1,4- Addition of HX To Dienes) but will not add to aromatic rings. Table of Contents 1. Reaction of Alkenes With Hydrohalic Acids (HCl, HBr, HI) When alkenes are treated with hydrohalic acids (HCl, HBr, or HI) they form alkyl halides. This is sometimes called hydrohalogenation of alkenes since it results in the addition of hydrogen and a halogen. In these addition reactions: the C-C pi bond and the H-X bond breaks; a new C-H and C-X bond forms (where X is Cl, Br, or I). If we add up the bond dissociation energies (BDE's) of the bonds that form (C-H, about 98 kcal/mol, and C-Cl, about 81 kcal/mol) and subtract their sum from those of the bonds that break (C-C pi, about 60 kcal/mol, and H-Cl, about 103 kcal/mol) the reaction is exothermic by about 18 kcal/mol for the addition of HCl. [Link to a useful table] Acid is required for these reactions to occur; no addition of halide to alkenes will happen in the absence of strong acid. (In other words, HCl = , but NaCl =). The new C-halogen bond tends to form on the most substituted carbon of the alkene (i.e. the one with the fewest carbons), and the new C-H bond tends to form on the carbon of the alkene containing the most hydrogens. 2. Markovnikov's Rule: Regioselectivity of HX Addition to Alkenes The reactions of alkenes with has been known for over 150 years. When an alkene is not symmetrical, the reaction has the potential to form two different constitutional isomers ("regioisomers"). However, in many cases, one constitutional isomer is formed in a much higher proportion than the other. In other words, the reaction is regioselective. In an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens. This has come to be known as "Markovnikov's Rule". Markovnikov's rule is what we would call an "empirical" rule. It was based purely on observed results, without any real underlying understanding of the mechanism of the reaction. In later years people had a hard time replicating Markovnikov's results with HBr, often finding that the least substituted regioisomer was formed instead! Later on, in the 1930s the cause of this aberrant regioselectivity was found to be the presence of peroxides in solvent, which led to a free-radical process for addition of H-Br to alkenes, which does not occur with H-I or H-Cl. See article – Free-Radical addition of H-Br to Alkenes. [Note 1] Subsequently we tend to say, for better or worse, that addition reactions to alkenes that follow this pattern (such as their reaction with H3O+) are "Markovnikov-selective", whereas reactions that follow the opposite pattern are "anti-Markovnikov selective" (such as hydroboration of alkenes). See if you can apply the pattern in the reaction of the alkene below (1-methylcyclopentene) with H-Cl. Click to Flip Another example is below. Draw the major product(s) and determine how they will be related: Click to Flip Can you work backwards to come up with the best starting material for this reaction? Click to Flip 3. Stereoselectivity (Or Lack Thereof) In Addition of HX To Alkenes When addition reactions occur across an alkene pi-bond, the (sp2-hybridized) trigonal planar carbons of the alkene are converted into (sp3-hybridized) tetrahedral carbons, and with this comes the potential for formation of stereoisomers. (See article: Types of Isomers) When the two new bonds to carbon are formed on the same face of the alkene, the addition is said to be "syn" When the two new bonds are formed on opposite faces of the alkene, the addition is said to be "anti". Addition reactions that give primarily syn or anti products are said to be stereoselective, and we will meet many examples in subsequent articles in this chapter (e.g. halogenation is stereoselective for anti products, and hydroboration is stereoselective for syn products). Addition of H-X to alkenes gives a mixture of syn addition products and anti addition products [Note 2]. In other words, the reaction is not particularly stereoselective. This lack of stereoselectivity leads to mixtures of syn and anti addition products, in some cases each as mixtures of enantiomers. See if you can draw the products of the reaction below: Click to Flip 4. Hydrohalogenation of Alkenes: The Mechanism Markovnikov was one of the more prominent chemists of his era, but back in 1870 he didn't know why the reaction tended to give the more substituted product. The first to really figure it out was Lucas in 1924 [Ref], based on observations that alkyl groups are more "electron releasing". After many decades it was finally proposed that reaction goes through an intermediate carbocation. (The existence of carbocations was a fairly controversial subject until the 1930's). In the first step, the alkene (a nucleophile) is protonated by strong acid, resulting in a new carbocation. [Note 3] Depending on where protonation occurs, two different carbocations may be formed. Being electron-poor species, carbocations are stabilized by adjacent electron-donating groups as well as by delocalization through resonance. (See article – 3 Factors Which Stabilize Carbocations). The transition state leading to the most stable carbocation will be lower in energy, which tends to be the most substituted carbocation. The arrow pushing for alkenes reacting with acids like H-X can be a little ambiguous – see Note 4. So it is ultimately this carbocation intermediate which is the underlying reason for why Markovnikov's rule is observed. Carbocations have an empty p-orbital and readily accept a pair of electrons from whatever Lewis bases happen to be present in solution. In the second step, the best nucleophile present (which tends to be the halide ion) then attacks the carbocation, forming the alkyl halide. To reiterate: Markovnikov went to his grave not knowing this mechanism. Heck, many chemists of his time didn't even accept that carbon was tetrahedral! So if you didn't figure this mechanism out immediately, that's to be expected and certainly nothing to feel bad about. The body of knowledge that is chemistry is built up of thousands of little experiments that eventually grew into the framework we have today. 5. Reaction Energy Diagram For Alkene Hydrohalogenation Sometimes it can be helpful to trace out the energy profile of a reaction as it progresses from starting material to products. In these diagrams, peaks (local maxima) are transition states and valleys (local minima) are intermediates. A simple hydrohalogenation reaction has two steps – each of which has a transition state – and a single carbocation intermediate. In the first step, our intrepid alkene is protonated by strong acid, resulting in the high-energy transition state TS 1. This step has the highest activation energy (the barrier between reactants and transition state) making it the rate-determining step for this reaction. From the transition state (TS1) energy maximum, the reaction proceeds to the carbocation intermediate. The second step involves attack of the halide nucleophile on the carbocation, which proceeds through transition state 2 (TS2). Note that the activation energy for this step is considerably less than for protonation of the alkene – in other words, it will be the fast step. The reaction then proceeds through TS2 to give the final product, the alkyl halide. 6. Carbocation Rearrangements – Hydride and Alkyl Shifts One key to the proposal of a carbocation intermediate was the observation that some hydrohalogenation reactions give products of carbocation rearrangements in addition to the expected addition product. For example when 4-methyl-1-butene was treated with HCl and allowed to sit at room temperature for an extended period, the product mixture was found to contain about half the expected Markovnikov addition product in addition to a new tertiary alkyl halide. [Ref] In this reaction the C-H bond that was originally part of the isopropyl group migrates to the secondary alkyl carbon. (See article – Rearrangements in Alkene Addition Reactions) See if you can draw a reasonable mechanism! Click to Flip These rearrangements can occur when a more stable carbocation can result from migration of a hydride or alkyl group. When a quaternary carbon is adjacent to a secondary carbocation, alkyl groups can migrate. Click to Flip Occasionally migrations between equivalently substituted groups can be favored, as in the example below. Click to Flip 7. Other Applications of Hydrohalogenation Alkynes will react with HX to give vinyl halides. A second equivalent of HX will give geminal dihalides. (For more, see Alkyne Hydrohalogenation) Dienes such as 1,3-butadiene will react with HX to give various products. See this article in the chapter on conjugated systems for more. (See article: 1,2- and 1,4-Addition of HX To Dienes) Aromatic rings such as benzene will not undergo addition reactions with HX. Aromatic rings tend to react through substitution. More in the chapter on aromatic rings. (See article: Introduction to Aromaticity) Carbocations are reactive intermediates and will readily combine with even poor Lewis bases. Sometimes those Lewis bases include other alkenes on the same molecule. This can result in cyclic molecules. For example, consider the reaction below: Click to Flip There are whole classes of molecules that are synthesized in nature via attack of alkenes on various carbocations. One of the most prominent classes is terpenes. I don't want to get into it in this article, but if you are looking for a good time, I strongly suggest looking at how the steroid skeleton of lanosterol is built up from the cyclization of squalene. [Note 5] This isn't the cyclization of an alkene, but it's another example of how rearrangements can occur in nature. In this example we start with alpha-pinene, one of the main ingredients in pine oil. Click to Flip 8. Summary HCl, HBr, and HI will all add to alkenes. The alkene acts as a nucleophile, forming a bond with the electrophilic proton of the acid. The reaction always occurs so as to form the most stable carbocation. This is responsible for the observations that led Markovnikov to postulate his rule in the first place. Be alert for the possibility of carbocation rearrangements when a more stable carbocation can be formed. This can sometimes even occur between carbons with similar substitution if it results in a resonance-stabilized carbocation. The reaction of HX with alkenes is essentially the same as the reaction of H3O+ with alkenes. They both follow what I call the Carbocation Pathway, one of the three key "buckets" of alkene reaction mechanisms that you might find helpful to remember. (See – Alkene Addition Reactions – The "Carbocation" Pathway) Notes Note 1. When peroxides (often written RO-OR) are present a very different reaction pathway occurs, where free-radical intermediates are involved. These reactions are anti-Markovnikov selective. For more on this reaction, see Free-Radical Addition of HBr To Alkenes. Note 2. Telling a small fib here, as this reaction does not always lack stereoselectivity. One particularly interesting set of results was in the addition of HBr to 1,2-dimethylcyclohexene in (the very non-polar solvent) pentane. It was found that addition occurred rapidly to give almost exclusively the trans product; letting it sit around for awhile led to some equilibration between stereoisomers. The authors propose that the reaction proceeds through a termolecular transition state (i.e. involving three molecules) with the alkene sandwiched between two molecules of HBr. Note 3. For our purposes, drawing the immediate formation of a carbocation is fine. Some studies look for the possibility of an even earlier intermediate called a "pi complex", where H+ is coordinated to the pi-bond. As the bond between the pi-bond to the proton becomes stronger, the pi-complex then evolves into the carbocation intermediate. Note 4. Alkenes present a little bit of a dilemma in using curved arrows to describe the movement of electron pairs, since the double bond is not polarized and there is no obvious nucleophilic or electrophilic end. The convention in drawing arrows is that the carbon involved in bond formation is the one closest to the electrophile. For example here is an example of arrow-pushing that shows the right-hand carbon of the double bond forming a new bond to H: And here is an example of curved arrows showing formation of a new bond to the left side of the alkene: To solve this dilemma, various new conventions have been devised such as the bouncy arrow formalism and drawing a dashed line to indicate the bond being formed, although these have not exactly taken the world by storm. Note 5. If you are looking for a good time, this review outlines the whole rich and fascinating history of "cationic" alkene cyclizations, with a particular focus on how steroids and other related compounds are synthesized in nature. Quiz Yourself! Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. (Advanced) References and Further Reading Ingold's "Structure and Mechanism in Organic Chemistry" is a valuable guide to the early literature on this topic. The Logic Behind Markovnikov's Rule: Was It an Inspired Guess? ...No! D. E. Lewis, Angew. Chem. Int. Ed. 2021, 60, 4412. DOI: 10.1002/anie.202008228 Fun, accessible historical essay examining Markovnikov's studies in the 1860's-1870's. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. Markownikoff, W. (1870) Justus Liebigs Ann. Chem., 153: 228-259. DOI: 10.1002/jlac.18701530204 The original Markovnikov paper. ELECTRON DISPLACEMENT IN CARBON COMPOUNDS I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS Howard J. Lucas and Archibald Y. Jameson Journal of the American Chemical Society 1924 46 (11), 2475-2482 DOI: 10.1021/ja01676a018 If not the earliest explanation of Markovnikov's rule, certainly one of them. Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane Frank C. Whitmore and Franklin Johnston Journal of the American Chemical Society 1933 55 (12), 5020-5022 DOI: 10.1021/ja01339a053 One of the first clearly written out explanations of a carbocation rearrangement in addition of HX to alkenes. A subsequent paper (JACS 1950 1511) goes into more detail. The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene George S. Hammond and Thomas D. Nevitt Journal of the American Chemical Society 1954 76 (16), 4121-4123 DOI: 10.1021/ja01645a020 OK. When I wrote, above, that the addition of HX to alkenes is not stereoselective, I fibbed. The truth is that it can be stereoselective for anti addition if carried out at low temperatures in non polar solvents such as pentane. The proposed mechanism is not a free carbocation but a termolecular transition state involving two equivalents of H-Br. (Interestingly, though, the reaction of H3O+ with the same compound is not stereoselective). In the strongly polar solvent acetic acid, the reaction results predominantly (but not exclusively!) through the classic carbocation mechanism. Hydrochlorination of cyclohexene in acetic acid. Kinetic and product studies Robert C. Fahey, Michael W. Monahan, and C. Allen McPherson Journal of the American Chemical Society 1970 92 (9), 2810-2815 DOI: 10.1021/ja00712a034 Detailed kinetic studies of the addition of HCl to cyclohexene in acetic acid, discussing a possible third-order mechanism (rate = k[cyclohexene][HX]2). SPIROANNELATION OF ENOL SILANES: 2-OXO-5-METHOXYSPIRO[5.4]DECANE Lee, T. V.; Porter, J. R. Org. Synth. 1995, 72, 189 DOI: 10.15227/orgsyn.072.0189 The first reaction in the above procedure involves two steps – addition of HBr across the double bond and converting the aldehyde to a dimethyl acetal. Markovnikov's Rule Robert C. Kerber Journal of Chemical Education 2007 84 (7), 1109 DOI: 10.1021/ed084p1109.1 A 2007 missive urging educators and textbook writers to retire the teaching of Markovnikov's Rule. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids Ryan A. Yoder and Jeffrey N. Johnston Chemical Reviews 2005 105 (12), 4730-4756 DOI: 10.1021/cr040623l Last updated: March 5th, 2025 | Hydrohalogenation of Alkenes and Markovnikov's Rule When hydrohalic acids (HCl, HBr, HI) are added to alkenes, addition reactions can occur, resulting in formation of a C-H and C-halogen bond and breakage of a C-C pi bond. The reaction tends to occur such that the halogen ends up attached to the carbon of the alkene attached to the fewest hydrogen atoms, a phenomenon known as Markovnikov's Rule. Addition of H-X to alkenes occurs through a protonation of the alkene to give a carbocation intermediate, followed by addition of the halide to the carbocation. A better reformulation of Markovnikov's rule is therefore that addition of HX to alkenes will proceed through the most stable carbocation, which is generally the more substituted carbon of the alkene. (Note that H-Br with peroxides (RO-OR) operates through a different reaction mechanism – see Free Radical Addition of H-Br to Alkenes). Carbocation rearrangements (hydride or alkyl shifts) can occur if they will result in a more stable carbocation intermediate. H-X will also add to alkynes (See: Addition of HX to alkynes) and dienes (See: 1,2- and 1,4- Addition of HX To Dienes) but will not add to aromatic rings. Table of Contents 1. Reaction of Alkenes With Hydrohalic Acids (HCl, HBr, HI) When alkenes are treated with hydrohalic acids (HCl, HBr, or HI) they form alkyl halides. This is sometimes called hydrohalogenation of alkenes since it results in the addition of hydrogen and a halogen. In these addition reactions: the C-C pi bond and the H-X bond breaks; a new C-H and C-X bond forms (where X is Cl, Br, or I). If we add up the bond dissociation energies (BDE's) of the bonds that form (C-H, about 98 kcal/mol, and C-Cl, about 81 kcal/mol) and subtract their sum from those of the bonds that break (C-C pi, about 60 kcal/mol, and H-Cl, about 103 kcal/mol) the reaction is exothermic by about 18 kcal/mol for the addition of HCl. [Link to a useful table] Acid is required for these reactions to occur; no addition of halide to alkenes will happen in the absence of strong acid. (In other words, HCl = , but NaCl =). The new C-halogen bond tends to form on the most substituted carbon of the alkene (i.e. the one with the fewest carbons), and the new C-H bond tends to form on the carbon of the alkene containing the most hydrogens. 2. Markovnikov's Rule: Regioselectivity of HX Addition to Alkenes The reactions of alkenes with has been known for over 150 years. When an alkene is not symmetrical, the reaction has the potential to form two different constitutional isomers ("regioisomers"). However, in many cases, one constitutional isomer is formed in a much higher proportion than the other. In other words, the reaction is regioselective. In an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens. This has come to be known as "Markovnikov's Rule". Markovnikov's rule is what we would call an "empirical" rule. It was based purely on observed results, without any real underlying understanding of the mechanism of the reaction. In later years people had a hard time replicating Markovnikov's results with HBr, often finding that the least substituted regioisomer was formed instead! Later on, in the 1930s the cause of this aberrant regioselectivity was found to be the presence of peroxides in solvent, which led to a free-radical process for addition of H-Br to alkenes, which does not occur with H-I or H-Cl. See article – Free-Radical addition of H-Br to Alkenes. [Note 1] Subsequently we tend to say, for better or worse, that addition reactions to alkenes that follow this pattern (such as their reaction with H3O+) are "Markovnikov-selective", whereas reactions that follow the opposite pattern are "anti-Markovnikov selective" (such as hydroboration of alkenes). See if you can apply the pattern in the reaction of the alkene below (1-methylcyclopentene) with H-Cl. Click to Flip Another example is below. Draw the major product(s) and determine how they will be related: Click to Flip Can you work backwards to come up with the best starting material for this reaction? Click to Flip 3. Stereoselectivity (Or Lack Thereof) In Addition of HX To Alkenes When addition reactions occur across an alkene pi-bond, the (sp2-hybridized) trigonal planar carbons of the alkene are converted into (sp3-hybridized) tetrahedral carbons, and with this comes the potential for formation of stereoisomers. (See article: Types of Isomers) When the two new bonds to carbon are formed on the same face of the alkene, the addition is said to be "syn" When the two new bonds are formed on opposite faces of the alkene, the addition is said to be "anti". Addition reactions that give primarily syn or anti products are said to be stereoselective, and we will meet many examples in subsequent articles in this chapter (e.g. halogenation is stereoselective for anti products, and hydroboration is stereoselective for syn products). Addition of H-X to alkenes gives a mixture of syn addition products and anti addition products [Note 2]. In other words, the reaction is not particularly stereoselective. This lack of stereoselectivity leads to mixtures of syn and anti addition products, in some cases each as mixtures of enantiomers. See if you can draw the products of the reaction below: Click to Flip 4. Hydrohalogenation of Alkenes: The Mechanism Markovnikov was one of the more prominent chemists of his era, but back in 1870 he didn't know why the reaction tended to give the more substituted product. The first to really figure it out was Lucas in 1924 [Ref], based on observations that alkyl groups are more "electron releasing". After many decades it was finally proposed that reaction goes through an intermediate carbocation. (The existence of carbocations was a fairly controversial subject until the 1930's). In the first step, the alkene (a nucleophile) is protonated by strong acid, resulting in a new carbocation. [Note 3] Depending on where protonation occurs, two different carbocations may be formed. Being electron-poor species, carbocations are stabilized by adjacent electron-donating groups as well as by delocalization through resonance. (See article – 3 Factors Which Stabilize Carbocations). The transition state leading to the most stable carbocation will be lower in energy, which tends to be the most substituted carbocation. The arrow pushing for alkenes reacting with acids like H-X can be a little ambiguous – see Note 4. So it is ultimately this carbocation intermediate which is the underlying reason for why Markovnikov's rule is observed. Carbocations have an empty p-orbital and readily accept a pair of electrons from whatever Lewis bases happen to be present in solution. In the second step, the best nucleophile present (which tends to be the halide ion) then attacks the carbocation, forming the alkyl halide. To reiterate: Markovnikov went to his grave not knowing this mechanism. Heck, many chemists of his time didn't even accept that carbon was tetrahedral! So if you didn't figure this mechanism out immediately, that's to be expected and certainly nothing to feel bad about. The body of knowledge that is chemistry is built up of thousands of little experiments that eventually grew into the framework we have today. 5. Reaction Energy Diagram For Alkene Hydrohalogenation Sometimes it can be helpful to trace out the energy profile of a reaction as it progresses from starting material to products. In these diagrams, peaks (local maxima) are transition states and valleys (local minima) are intermediates. A simple hydrohalogenation reaction has two steps – each of which has a transition state – and a single carbocation intermediate. In the first step, our intrepid alkene is protonated by strong acid, resulting in the high-energy transition state TS 1. This step has the highest activation energy (the barrier between reactants and transition state) making it the rate-determining step for this reaction. From the transition state (TS1) energy maximum, the reaction proceeds to the carbocation intermediate. The second step involves attack of the halide nucleophile on the carbocation, which proceeds through transition state 2 (TS2). Note that the activation energy for this step is considerably less than for protonation of the alkene – in other words, it will be the fast step. The reaction then proceeds through TS2 to give the final product, the alkyl halide. 6. Carbocation Rearrangements – Hydride and Alkyl Shifts One key to the proposal of a carbocation intermediate was the observation that some hydrohalogenation reactions give products of carbocation rearrangements in addition to the expected addition product. For example when 4-methyl-1-butene was treated with HCl and allowed to sit at room temperature for an extended period, the product mixture was found to contain about half the expected Markovnikov addition product in addition to a new tertiary alkyl halide. [Ref] In this reaction the C-H bond that was originally part of the isopropyl group migrates to the secondary alkyl carbon. (See article – Rearrangements in Alkene Addition Reactions) See if you can draw a reasonable mechanism! Click to Flip These rearrangements can occur when a more stable carbocation can result from migration of a hydride or alkyl group. When a quaternary carbon is adjacent to a secondary carbocation, alkyl groups can migrate. Click to Flip Occasionally migrations between equivalently substituted groups can be favored, as in the example below. Click to Flip 7. Other Applications of Hydrohalogenation Alkynes will react with HX to give vinyl halides. A second equivalent of HX will give geminal dihalides. (For more, see Alkyne Hydrohalogenation) Dienes such as 1,3-butadiene will react with HX to give various products. See this article in the chapter on conjugated systems for more. (See article: 1,2- and 1,4-Addition of HX To Dienes) Aromatic rings such as benzene will not undergo addition reactions with HX. Aromatic rings tend to react through substitution. More in the chapter on aromatic rings. (See article: Introduction to Aromaticity) Carbocations are reactive intermediates and will readily combine with even poor Lewis bases. Sometimes those Lewis bases include other alkenes on the same molecule. This can result in cyclic molecules. For example, consider the reaction below: Click to Flip There are whole classes of molecules that are synthesized in nature via attack of alkenes on various carbocations. One of the most prominent classes is terpenes. I don't want to get into it in this article, but if you are looking for a good time, I strongly suggest looking at how the steroid skeleton of lanosterol is built up from the cyclization of squalene. [Note 5] This isn't the cyclization of an alkene, but it's another example of how rearrangements can occur in nature. In this example we start with alpha-pinene, one of the main ingredients in pine oil. Click to Flip 8. Summary HCl, HBr, and HI will all add to alkenes. The alkene acts as a nucleophile, forming a bond with the electrophilic proton of the acid. The reaction always occurs so as to form the most stable carbocation. This is responsible for the observations that led Markovnikov to postulate his rule in the first place. Be alert for the possibility of carbocation rearrangements when a more stable carbocation can be formed. This can sometimes even occur between carbons with similar substitution if it results in a resonance-stabilized carbocation. The reaction of HX with alkenes is essentially the same as the reaction of H3O+ with alkenes. They both follow what I call the Carbocation Pathway, one of the three key "buckets" of alkene reaction mechanisms that you might find helpful to remember. (See – Alkene Addition Reactions – The "Carbocation" Pathway) Notes Note 1. When peroxides (often written RO-OR) are present a very different reaction pathway occurs, where free-radical intermediates are involved. These reactions are anti-Markovnikov selective. For more on this reaction, see Free-Radical Addition of HBr To Alkenes. Note 2. Telling a small fib here, as this reaction does not always lack stereoselectivity. One particularly interesting set of results was in the addition of HBr to 1,2-

dimethylcyclohexene in (the very non-polar solvent) pentane. It was found that addition occurred rapidly to give almost exclusively the trans product; letting it sit around for awhile led to some equilibration between stereoisomers. The authors propose that the reaction proceeds through a termolecular transition state (i.e. involving three molecules) with the alkene sandwiched between two molecules of HBr. Note 3. For our purposes, drawing the immediate formation of a carbocation is fine. Some studies look for the possibility of an even earlier intermediate called a “pi complex”, where H+ is coordinated to the pi-bond. As the bond between the pi-bond to the proton becomes stronger, the pi-complex then evolves into the carbocation intermediate. Note 4. Alkenes present a little bit of a dilemma in using curved arrows to describe the movement of electron pairs, since the double bond is not polarized and there is no obvious nucleophilic or electrophilic end. The convention in drawing arrows is that the carbon involved in bond formation is the one closest to the electrophile. For example here is an example of arrow-pushing that shows the right-hand carbon of the double bond forming a new bond to H: And here is an example of curved arrows showing formation of a new bond to the left side of the alkene: To solve this dilemma, various new conventions have been devised such as the bouncy arrow formalism and drawing a dashed line to indicate the bond being formed, although these have not exactly taken the world by storm. Note 5. If you are looking for a good time, this review outlines the whole rich and fascinating history of “cationic” alkene cyclizations, with a particular focus on how steroids and other related compounds are synthesized in nature. Quiz Yourself! Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. Become a MOC member to see the clickable quiz with answers on the back. (Advanced) References and Further Reading Ingold’s “Structure and Mechanism in Organic Chemistry” is a valuable guide to the early literature on this topic. The Logic Behind Markovnikov’s Rule: Was It an Inspired Guess? ...No! D. E. Lewis, Angew. Chem. Int. Ed. 2021, 60, 4412. DOI: 10.1002/anie.202008228 Fun, accessible historical essay examining Markovnikov’s studies in the 1860’s-1870’s. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. Markownikoff, W. (1870) Justus Liebigs Ann. Chem., 153: 228-259. DOI: 10.1002/jlac.18701530204 The original Markovnikov paper. ELECTRON DISPLACEMENT IN CARBON COMPOUNDS I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS Howard J. Lucas and Archibald Y. Jameson Journal of the American Chemical Society 1924 46 (11), 2475-2482 DOI: 10.1021/ja01676a018 If not the earliest explanation of Markovnikov’s rule, certainly one of them. Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane Frank C. Whitmore and Franklin Johnston Journal of the American Chemical Society 1933 55 (12), 5020-5022 DOI: 10.1021/ja01339a053 One of the first clearly written out explanations of a carbocation rearrangement in addition of HX to alkenes. A subsequent paper (JACS 1950 1511) goes into more detail. The Stereochemistry of the Addition of Hydrogen Bromide to 1,2-Dimethylcyclohexene George S. Hammond and Thomas D. Nevitt Journal of the American Chemical Society 1954 76 (16), 4121-4123 DOI: 10.1021/ja01645a020 OK. When I wrote, above, that the addition of HX to alkenes is not stereoselective, I fibbed. The truth is that it can be stereoselective for anti addition if carried out at low temperatures in non polar solvents such as pentane. The proposed mechanism is not a free carbocation but a termolecular transition state involving two equivalents of H-Br. (Interestingly, though, the reaction of H3O+ with the same compound is not stereoselective). In the strongly polar solvent acetic acid, the reaction results predominantly (but not exclusively!) through the classic carbocation mechanism. Hydrochlorination of cyclohexene in acetic acid. Kinetic and product studies Robert C. Fahey, Michael W. Monahan, and C. Allen McPherson Journal of the American Chemical Society 1970 92 (9), 2810-2815 DOI: 10.1021/ja00712a034 Detailed kinetic studies of the addition of HCl to cyclohexene in acetic acid, discussing a possible third-order mechanism (rate = k[cyclohexene][HX]2). SPIROANNELATION OF ENOL SILANES: 2-OXO-5-METHOXYSPIRO[5.4]DECANE Lee, T. V.; Porter, J. R. Org. Synth. 1995, 72, 189 DOI: 10.15227/orgsyn.072.0189 The first reaction in the above procedure involves two steps – addition of HBr across the double bond and converting the aldehyde to a dimethyl acetal. Markovnikov’s Rule Robert C. Kerber Journal of Chemical Education 2007 84 (7), 1109 DOI: 10.1021/ed084p1109.1 A 2007 missive urging educators and textbook writers to retire the teaching of Markovnikov’s Rule. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids Ryan A. Yoder and Jeffrey N. Johnston Chemical Reviews 2005 105 (12), 4730-4756 DOI: 10.1021/cr040623l Double bonds are electron-rich and therefore they react with many electron-deficient species including acids such as HCl, HBr, and HI. The products of these addition reactions of HX acids to alkenes are alkyl halides: These are hydrohalogenation reactions which are a type of electrophilic addition reactions to alkenes. The electrophile here is the acid or other molecules that react with the alkene. The alkene can be classified as a Lewis base as it is the electron donor, and it also falls in the category of Brønsted bases because, in these particular reactions, it is also the proton acceptor. We will see, when discussing the mechanism of these reactions, that it is the π bond that acts as a base, and although it is not a strong base, it is still reactive to strong acids. The Regiochemistry of Hydrohalogenation of Alkenes The most important feature of these reactions, applicable in synthesis, is their regiochemistry. Notice how in the third and fourth reactions, the I and Br appeared on the more substituted carbon atoms (secondary in the case of I, and tertiary in the case of Br). This selectivity can be explained by showing the mechanism of the hydrogen halide additions to alkenes. The rate-determining step of the electrophilic addition of HX acids to alkenes is the first step where the electrons of the π bond attack the hydrogen of the acid, forming a carbocation intermediate. This step defines the product of the reaction as every double bond can be “opened up in two ways, depending on which carbon makes the new C-H bond. For example, in the third reaction, but-1-ene can break the double bond either to the left or to the right, leading to a secondary or a tertiary carbocation: To predict which carbocation is favored, we need to compare their stability. What do you remember about the stability of carbocations? Because of electron-donating and hyperconjugation, the stability of carbocations increases with the number of alkyl groups connected to the positively charged carbon: Therefore, the secondary carbocation is the preferred intermediate in this reaction, and, upon formation, it is quickly attacked by the halide anion giving the corresponding alkyl halide as the final product: Notice that the product is formed as a mixture of two enantiomers in equal quantities (racemic mixture). This is the stereochemistry of the hydrohalogenation which will discuss later in this post. Let’s also go back a little bit to address the first two reactions: The alkene in the first reaction is symmetrical, and regardless of what carbon the Br adds to, we are going the same product. It is a racemic mixture of two enantiomers, as 2-bromobutane is a chiral compound, but there is no regiochemistry in addition reactions to symmetrical alkenes. In the second reaction, we have pent-2-ene, and it is not symmetrical. On one end of the double bond, there is a methyl and on the other end, there is an ethyl group. And even though methyl is a smaller group than ethyl, and one may expect to see some preference of Br adding to the less sterically hindered carbon, little or no regioselectivity is observed in hydrogen halide additions to alkenes with different sizes of alkyl groups. To summarize the regiochemistry of HX addition reactions to alkenes, remember that the halogen adds to the more substituted carbon of the double bond. We can also say that the hydrogen adds to the less substituted carbon of the double bond or which the same to the carbon that already has more hydrogens. This is known as the Markovnikov’s rule, and we are going to see it quite often in the reactions of alkenes. Rearrangements in Hydrohalogenation of Alkenes The formation of carbocation intermediates brings the possibility of rearrangements during hydrohalogenation of alkenes, just like we have seen in SN1 and E1 reactions. For example, when the following alkene is treated with HBr, based on the Markovnikov’s rule, we may expect the Br to add to the middle carbon because of the greater stability of the secondary carbocation: So, how does this happen? In the first step, we know that the hydrogen addition will form a secondary carbocation because it is more stable than the possible primary carbocation. This is true, upon protonation, the secondary carbocation is formed; however, before reacting with the bromide ion, it undergoes a 1,2-hydride shift rearrangement to form a more stable tertiary carbocation: Once the tertiary carbocation is formed, it is attacked by the bromide resulting in a tertiary alkyl halide as the major product of the reaction: Let’s combine the steps in one scheme to represent the mechanism of hydride shift rearrangement in the hydrohalogenation of alkenes: Rearrangements during hydrohalogenation of alkenes, and other reactions going via carbocation intermediates, can also happen via 1,2-methyl (more accurately methide) shifts. For example, instead of the hydrogen, there was a methyl group on the alkene we discussed above, a 1,2-methyl shift would occur to transform the secondary carbocation to a more stable tertiary carbocation: To summarize this section, remember that, when possible, rearrangements are going to happen. Therefore, you need to keep them in mind when looking at any reaction involving a carbocation intermediate. In a typical undergraduate organic chemistry course, these are going to be SN1, E1, and the electrophilic addition reactions to alkenes such as those of hydrohalic acids (hydrogen halides), and acid-catalyzed hydration. The Stereochemistry of Hydrohalogenation of Alkenes There is no stereoselectivity in the addition of acids to alkenes. Let’s see what products are formed when the alkene has no chirality centers. Hydrohalogenation of Alkenes with No Chirality Centers For example, in the following addition reaction of HCl to the unsymmetrical alkene, we obtain a mixture of enantiomers which means the reaction is not selective to any of these stereoisomers: To summarize, addition reactions of alkenes with no stereogenic center that form a product with one stereogenic center produce a racemic mixture of enantiomers. This is explained by the fact that carbocations are sp2-hybridized, flat centers (we are talking about the positively charged carbon) and the nucleophilic attack occurs from both sides: This attack happens in the same amounts and as a result, a racemic mixture of two enantiomers is obtained. Hydrohalogenation of Alkenes with a Chirality Center If the starting alkene contains a chirality center, and the addition to the double bond creates a new chirality center, then the products are diastereomers: The asymmetric center in the starting material is not changed since it does not participate in the reaction. The new asymmetric center, however, is opposite for each product depending on the face the bromide had attacked the carbocation. Therefore, the products are a mixture of diastereomers. Similar to this, SN1 reactions can also produce diastereomers even though we usually say that they give a racemic mixture. You can check problems 3.5 and 3.6. Addition Reactions that Form a Product with Two Chirality Centers Let’s consider the reaction of 1,2-dimethylcyclohexene with HBr. The starting material does not have any asymmetric centers. However, it produces four stereoisomers in this reaction! Let’s see how this happens and what is the relationship between these stereoisomers. The first step is, as usual, the protonation of the double bond and what is important here is to remember/visualize that the H can add from both faces of the double bond: Notice that because of the hydrogen adding from different faces, the new chirality canter can be either R or S, and statistically it forms in a 50:50 ratio. There is no preference as to hydrogen adding from one side or the other side – no stereoselectivity. Similar to this, once the carbocation is formed, the bromide ion attacks the positively charged, trigonal planar carbon from above or below. This variety of additions results in four stereoisomers as final products. These are pairs of enantiomers and each enantiomer has two diastereomers: There is no control over the stereochemistry of this reaction and the proton, as well as the bromide (or any other substituent), add from both sides in equal amounts. Therefore, the reaction is not stereoselective i.e. none of the stereoisomers is formed preferentially. It is also not stereospecific, as the same products are obtained regardless if the cis or trans stereoisomers of the alkene are used. Therefore, when two stereogenic centers are formed in an addition reaction of alkenes, all the possible stereoisomers are formed, and the product is a mixture of enantiomers and diastereomers. Syn and Anti Additions to Alkenes Labeling the addition as “Above” and “Below’ is not scientific and not accurate either as the direction depends on the viewer. Therefore, a more universal approach is used to describe the stereochemistry of additions to the double bond. When two groups add to the same side of the double bond, it is called a syn addition and when they add from different sides, it is an anti addition. The hydrohalogenation of alkenes occurs both via syn and anti addition. A representative example of a syn addition to alkenes would be the hydroboration-oxidation reaction where the H and OH groups are adding to the same side of the double bond. The reaction, however, is going with a different mechanism; there are no ionic intermediates and it is a concerted mechanism: A good example of an anti addition is the dihydroxylation reaction by peroxy acids. Notice how the H and OH groups appear on opposite sides in the product. Check Also Share — copy and redistribute the material in any medium or format for any purpose, even commercially. Adapt — remix, transform, and build upon the material for any purpose, even commercially. The licensor cannot revoke these freedoms as long as you follow the license terms. Attribution — You must give appropriate credit , provide a link to the license, and indicate if changes were made . You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use. ShareAlike — If you remix, transform, or build upon the material, you must distribute your contributions under the same license as the original. No additional restrictions — You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits. You do not have to comply with the license for elements of the material in the public domain or where your use is permitted by an applicable exception or limitation . No warranties are given. The license may not give you all of the permissions necessary for your intended use. For example, other rights such as publicity, privacy, or moral rights may limit how you use the material. Reaction Overview: The hydrohalogenation of alkenes involves breaking a carbon to carbon double bond, followed by the electrophilic addition of a hydrogen atom and halogen. The halide will add to the more substituted carbon following Markovnikov's rule. The product is a haloalkane also called an alkyl halide. Summary of Hydrohalogenation Mechanism Nucleophilic pi bond reaches for electrophilic H in H-X, pi bond breaks in the process H adds to the less substituted carbon atom following Markovnikov's rule More substituted carbon is now deficient getting a formal charge of +1 Negative halide in solution attacks the carbocation forming a bond Product is a haloalkane – also known as alkyl halide Mechanism Overview and Explanation (watch my Hydrohalogenation video to see the detailed step-by-step mechanism in action) Key Reaction Notes: This reaction has a carbocation intermediate and therefore follows Markovnikov's rule Look out for carbocation rearrangements This reaction must be carried out in an ‘inert' solvent This reaction is regioselective – halide adds to more substituted carbon Mechanism for hydrohalogenation with a hydride-shift (carbocation rearrangement) What's Really Going On In This Reaction? Hydrohalogenation, an electrophilic alkene addition reaction, is highly useful as a precursor reaction in multi-step organic chemistry synthesis. Understanding the Molecules: H-X molecules such as H-I, H-Br and H-Cl are highly polar molecules. The halogen is highly electronegative and will ‘hog' the electrons between itself and hydrogen. This concentration of electrons on the halogen makes it partially negative, while pulling the electrons away from hydrogen makes H partially positive. (You will seldom see this reaction for H-F due to fluorine's high electronegativity and poor reactivity) Unlike sigma (single) bonding electrons, the pi bond sits very high and very low on the carbon skeleton. This allows it to be easily ‘distracted' by other nearby molecules. These electrons are highly nucleophilic (attracted to positive) and will reach out for a passing electrophile (positive or partially positive). Breaking The Pi Bond: When an H-X bond such as H-Cl or H-Br gets close to the alkene, the pi bonds will reach out to grab the partially positive hydrogen atom. In order to form this bond, one of the pi electrons must let go of the carbon atom that it's bound to. In deciding which carbon atom we must follow Markovnikov's rule and ask ourselves which pi bond is more capable of holding a positive charge. The more substituted the carbon atom, the more stable the resulting carbocation. The other carbon atom hasn't let go of its pi electrons and is now singly bound to the hydrogen atom. This is how the less substituted carbon atom winds up bound to hydrogen. The hydrogen atom is capable of forming just a single bond. As it forms a bond with carbon it must let go of the halogen. This allows the halogen to grab the electrons that used to bind it to hydrogen, and float away in solution with a complete octet and negative charge. Attack of the Halide: Negative halogens are nucleophiles. Nucleophiles are attracted to electrophiles (positive charges). The lone halogen will use one of it's lone electron pairs to attack the carbocation forming a sigma bond. Since the carbocation was on the more substituted carbon, the halogen winds up attached at the more substituted carbon as well. Purpose Of Inert Solvent: The choice of solvent will make a big difference in the overall reaction. Think of your inert solvents as ‘I don't care' solvents. They serve the single purpose of dissolving the reactants and reagents, but they don't interfere in the actual process. Inert solvents for this reaction include CH_2Cl_2, CCl_4 and more. Notice that they are NOT polar protic. The use of a non-inert solvent or polar protic solvent like water will result in a very different reaction. At the point where the halide breaks away from hydrogen, the solvent ‘butts in'. The polar protic solvent will use its partially positive hydrogen atoms to surround or ‘cage' the negative halogen. This prevents the halogen from attacking the carbocation. Instead, one of the polar protic solvent molecules will use a lone pair of electrons to attack the carbocation. For example, if carried out in water, the final product will be an alcohol. If carried out in alcohol the product will be an ether. See the hydrohalogenation reaction come to life along with a few practice examples in my alkene halogenation video: