

## 7.8: ELECTROPHILIC ADDITION REACTIONS OF ALKENES

### OBJECTIVES

After completing this section, you should be able to

- explain the term “electrophilic addition reaction,” using the reaction of a protic acid, HX, with an alkene as an example.
- write the mechanism for the reaction of a protic acid, HX, with an alkene.
- sketch a reaction energy diagram for the electrophilic addition of an acid, HX, to an alkene.

### KEY TERMS

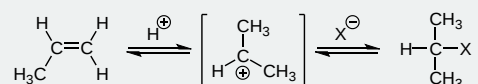
Make certain that you can define, and use in context, the key terms below.

- carbocation (carbonium ion)
- electrophilic addition reaction

### STUDY NOTES

An *electrophilic addition reaction* is a reaction in which a substrate is initially attacked by an electrophile, and the overall result is the addition of one or more relatively simple molecules across a multiple bond.

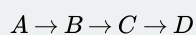
The mechanism for the addition of hydrogen halide to propene shown in the reading is quite detailed. Normally, an organic chemist would write the reaction scheme as follows:



However, the more detailed mechanism shown in the reading does allow you to see the exact fate of all the electrons involved in the reaction.

In your previous chemistry course, you were probably taught the importance of balancing chemical equations. It may come as a surprise to you that organic chemists usually do not balance their equations, and often represent reactions using a format which is quite different from the carefully written, balanced equations encountered in general chemistry courses. In fact, organic chemists are rarely interested in the inorganic products of their reactions; furthermore, most organic reactions are non-quantitative in nature.

In many of the reactions in this course, the percentage yield is indicated beneath the products: you are not expected to memorize these figures. The question of yield is very important in organic chemistry, where two, five, ten or even twenty reactions may be needed to synthesize a desired product. For example, if a chemist wishes to prepare compound D by the following reaction sequence:



and each of the individual steps gives only a 50% yield, one mole of A would give only

$$1 \text{ mol} \times \frac{50\%}{100\%} \times \frac{50\%}{100\%} \times \frac{50\%}{100\%} = 0.125 \text{ mol of D}$$

You will gain first-hand experience of such situations in the laboratory component of this course.

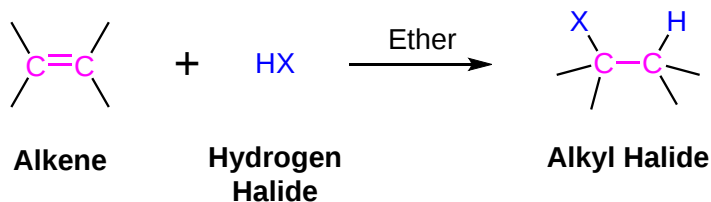
### INTRODUCTION

One of the most important reactions for alkenes is called electrophilic addition. In this chapter several variations of the electrophilic addition reaction will be discussed. Each case will have aspects common among all electrophilic addition. In this section, the electrophilic addition reaction will be discussed in general to provide a better understanding of subsequent alkene reactions.

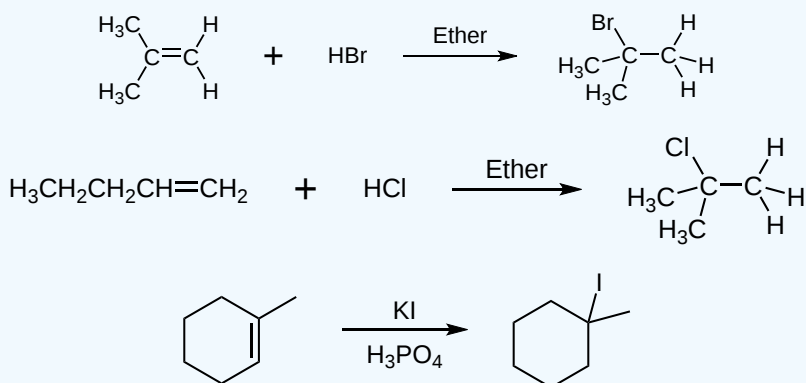
As discussed in Section 6-5, the double bond in alkenes is electron rich due to the presence of 4 electrons instead of the two in a single bond. Also, the pi electrons are positioned above and below the double bond making them more accessible for reactions. Overall, double bonds can easily donate lone pair electrons to act like a nucleophile (nucleus-loving, electron rich, a Lewis acid). During an electrophilic addition reactions double bonds donate lone pair electrons to an electrophile (Electron-loving, electron poor, a Lewis base). There are many types of electrophilic addition, but this section will focus on the addition of hydrogen halides (HX). Many of the basic ideas discussed will be applicable to subsequent electrophilic addition reactions.

## GENERAL REACTION

Overall during this reaction the pi bond of the alkene is broken to form two single, sigma bonds. As shown in the reaction mechanism, one of these sigma bonds is connected to the H and the other to the X of the hydrogen halide. This reaction works well with HBr and HCl. HI can also be used but is usually generated during the reaction by reacting potassium iodide (KI) with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>).



### ✓ EXAMPLE 7.8.1



## ADDITION TO SYMMETRICAL ALKENES

### What happens?

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other.

For example, with ethene and hydrogen chloride, you get chloroethane:



Figure 7.8.1 Electrophilic addition of HCl to ethene.

With but-2-ene you get 2-chlorobutane:

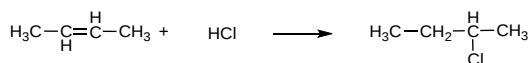


Figure 7.8.2 Electrophilic addition of HCl to but-2-ene.

What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different if the alkene was unsymmetrical - that's why we have to look at them separately.

## MECHANISM

### Step 1) Electrophilic Attack

During the first step of the mechanism, the 2 pi electrons from the double bond attack the H in the HBr electrophile which is shown by a curved arrow. The two pi electrons form a C-H sigma bond between the hydrogen from HBr and a carbon from the double bond. Simultaneously the electrons from the H-X bond move onto the halogen to form a halide anion. The removal of pi electrons from the double bond makes one of the carbons become an electron deficient carbocation intermediate. This carbon is sp<sup>2</sup> hybridized and the positive charge is contained in an unhybridized p orbital.

## Step 2) Nucleophilic attack by halide anion

The formed carbocation now can act as an electrophile and accept an electron pair from the nucleophilic halide anion. The electron pair becomes a X-C sigma bond to create the neutral alkyl halide product of electrophilic addition.

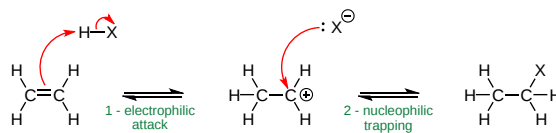


Figure 7.8.3 Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene

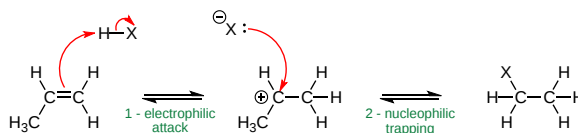
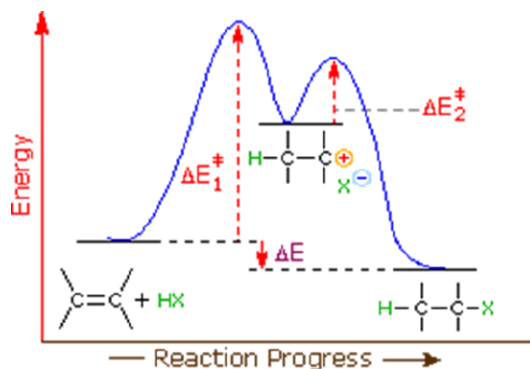


Figure 7.8.4 Mechanism of Electrophilic Addition of Hydrogen Halide to Propene

All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

## REACTION ENERGY DIAGRAM

An energy diagram for the two-step electrophilic addition mechanism is shown below. The energy diagram has two peaks which represent the transition state for each mechanistic step. The peaks are separated by a valley which represents the high energy carbocation reaction intermediate. Because the energy of activation for the first step of the mechanism ( $\Delta E^\ddagger_1$ ) is much larger than the second ( $\Delta E^\ddagger_2$ ), the first step of the mechanism is the rate-determining step. Both the alkene and the hydrogen halide are reactants in the first step of the mechanism, this electrophilic addition is a second order reaction and the rate law expression can be written  $\text{rate} = k[\text{Alkene}][\text{HX}]$ . Also, any structural feature which can stabilize the transition state between the reactants the carbocation intermediate will lower  $\Delta E^\ddagger_1$  and thereby increase the reaction rate. Overall, the alkyl halide product of this reaction more stable than the reactants making the reaction exothermic.



## REACTION RATES

### Variation of rates when you change the halogen

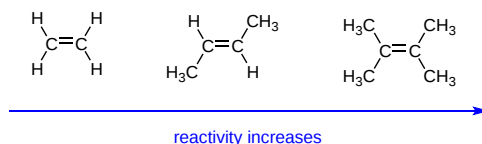
Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions.

When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

### Variation of rates when you change the alkene

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be.

Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond. For example:

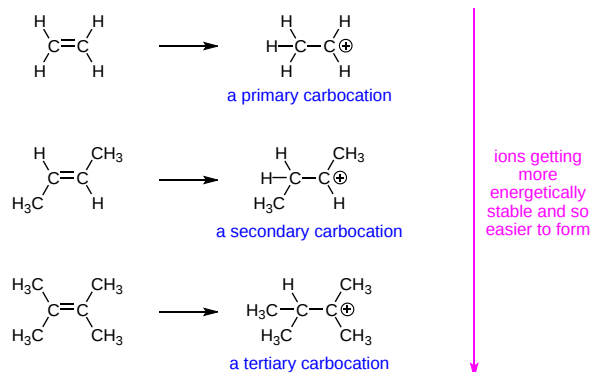


There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this.

Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes. The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride.

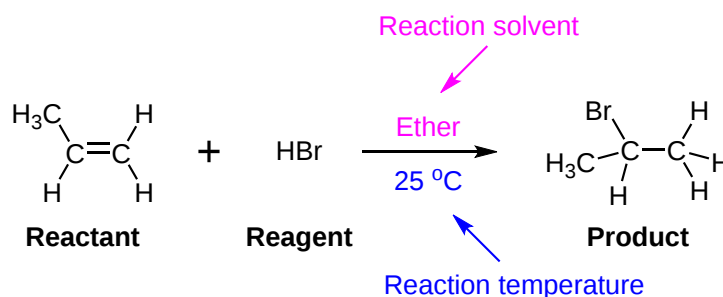
The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



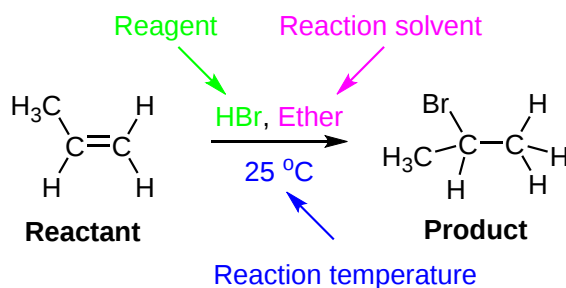
The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

## REPRESENTING ORGANIC REACTIONS

Organic reaction equations are often written in one of two ways. The reactant for the reaction is written to the left of the reaction arrow. The products are written to the right of the arrow. The reagent for the reaction is written above the arrow. Other reaction conditions such as the solvent or the temperature can be written above or below the reaction arrow.



Alternatively the reactant and reagent can both be written to the left of the reaction arrow. This is typically done to highlight the importance of the reactant. The solvent and reaction temperature are still written above or below the reaction arrow. The reaction products are still written to the right of the reaction arrow.



This page titled 7.8: Electrophilic Addition Reactions of Alkenes is shared under a CC BY-SA 4.0 license and was authored, remixed, and/or curated by Jim Clark, Steven Farmer, Dietmar Kennepohl, Krista Cunningham, Tim Soderberg, William Reusch, John Roberts, Marjorie C. Caserio, & Marjorie C. Caserio.

- [7.8: Electrophilic Addition Reactions of Alkenes](#) by Dietmar Kennepohl, Jim Clark, John Roberts, Krista Cunningham, Marjorie C. Caserio, Steven Farmer, Tim Soderberg, William Reusch is licensed [CC BY-SA 4.0](#).