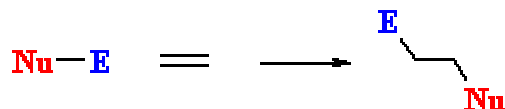


Electrophilic Addition Reactions



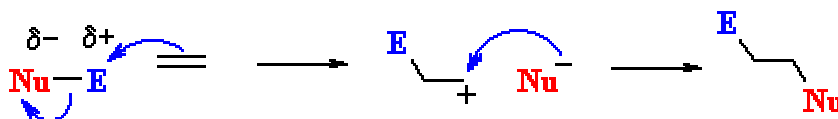
Electrophilic addition reactions are an important class of reactions that allow the interconversion of $C=C$ and $C\equiv C$ into a range of important functional groups.

Conceptually, addition is the reverse of elimination

What does the term "*electrophilic addition*" imply ?

A **electrophile**, E^+ , is an electron poor species that will react with an electron rich species (the $C=C$)

An **addition** implies that two systems combine to a single entity.



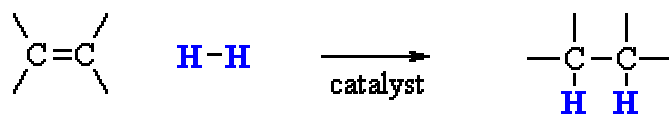
Depending on the relative timing of these events, slightly different mechanisms are possible:

- Reaction of the $C=C$ with E^+ to give a carbocation (or another cationic intermediate) that then reacts with a Nu^-
- Simultaneous formation of the two σ bonds

The following pointers may aid your understanding of these reactions:

- Recognise the **electrophile** present in the reagent combination
- The **electrophile** adds first to the alkene, dictating the **regioselectivity**.
- If the reaction proceeds via a planar carbocation, the reaction is **not stereoselective**
- If the two new σ bonds form at the **same** time from the **same species**, then **syn** addition is observed
- If the two new σ bonds form at **different** times from **different species**, then **anti** addition is observed

Hydrogenation of Alkenes



Reaction Type: Electrophilic Addition

Summary

- Alkenes can be reduced to alkanes with H_2 in the presence of metal catalysts such as Pt, Pd, Ni or Rh.
- The two new C-H σ bonds are formed simultaneously from H atoms absorbed into the metal surface.
- The reaction is **stereospecific** giving only the *syn* addition product.
- This reaction forms the basis of experimental "*heats of hydrogenation*" which can be used to establish the stability of isomeric alkenes.

CATALYTIC HYDROGENATION

Step 1:

Hydrogen gets absorbed onto the metal surface.



Step 2:

Alkene approaches the H atoms absorbed on the metal surface.

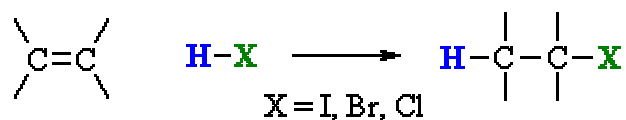


Step 3:

C=C reacts with the H atoms on the surface forming the two new C-H σ bonds.



Reaction of Alkenes with Hydrogen Halides



Reaction type: Electrophilic Addition

Summary

- When treated with HX alkenes form alkyl halides.
- Hydrogen halide reactivity order : $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (paralleling acidity order).
- Regioselectivity predicted by **Markovnikov's rule** :
"For addition of hydrogen halides to alkenes, the H atom adds to the C with the most H atoms already present"
- Reaction proceeds via protonation to give the more stable [carbocation intermediate](#).
- Not stereoselective since reaction proceeds via planar carbocation.

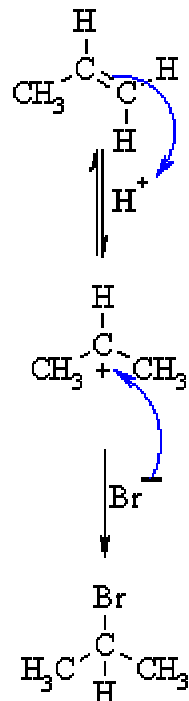
MECHANISM FOR REACTION OF ALKENES WITH HBr

Step 1:

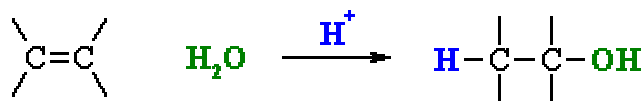
An acid/base reaction. Protonation of the alkene to generate the more stable carbocation. The π electrons act pairs as a Lewis base.

Step 2:

Attack of the nucleophilic bromide ion on the electrophilic carbocation creates the alkyl bromide.



Hydration of Alkenes



Reaction type: Electrophilic Addition

MECHANISM FOR REACTION OF ALKENES WITH H_3O^+

Step 1:

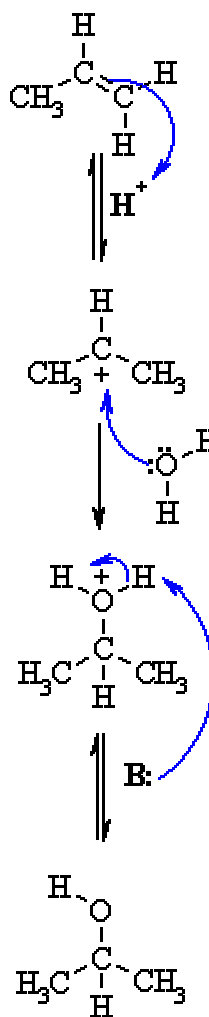
An acid / base reaction. Protonation of the alkene to generate the more stable carbocation. The π electrons act as a Lewis base.

Step 2:

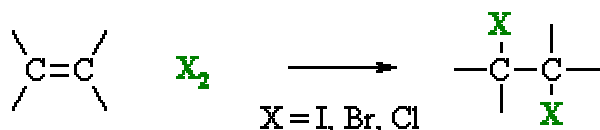
Attack of the nucleophilic water molecule on the electrophilic carbocation creates an oxonium ion.

Step 3:

An acid / base reaction. Deprotonation by a base generates the alcohol and regenerates the acid catalyst.



Halogenation of Alkenes



Reaction type: Electrophilic Addition

Summary

- Overall transformation : $\text{C}=\text{C}$ to $\text{X}-\text{C}-\text{C}-\text{X}$
- Reagent : normally the halogen (*e.g.* Br_2) in an inert solvent like methylene chloride, CH_2Cl_2 .
- Regioselectivity : not relevant since both new bonds are the same, $\text{C}-\text{X}$.
- Reaction proceeds via cyclic halonium ion.
- Stereoselectivity : **anti** since the two $\text{C}-\text{X}$ bonds form in separate steps one from X_2 the other X^- .

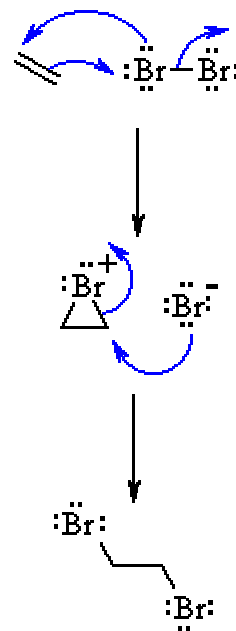
MECHANISM FOR REACTION OF ALKENES WITH HALOGENS

Step 1:

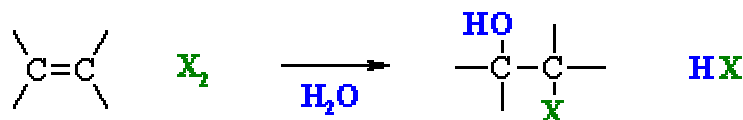
The π electrons act as a nucleophile, attacking the bromine, displacing a bromide ion but forming a cationic cyclic bromonium ion as an intermediate.

Step 2:

Attack of the nucleophilic bromide from the side away from the bromonium center in an $\text{S}_{\text{N}}2$ like fashion opens the cyclic bromonium ion to give overall *trans* addition.



Halohydrin formation of Alkenes



Reaction type: Electrophilic Addition

- Regioselectivity : **X** reacts as the electrophile so the C-O bond forms at the more stable cation center.
- Stereoselectivity : **anti** since the two new σ bonds form in separate steps.

MECHANISM FOR REACTION OF ALKENES WITH $\text{Br}_2 / \text{H}_2\text{O}$

Step 1:

Same first step as for the reaction of $\text{Br}_2/\text{CH}_2\text{Cl}_2$.

The π electrons act as a nucleophile, attacking the bromine, displacing a bromide ion but forming a cationic cyclic bromonium ion as an intermediate.

Step 2:

Attack of the nucleophilic water molecule from the side away from the bromonium center in an $\text{S}_\text{N}2$ like fashion opens the cyclic bromonium ion to give overall *trans* addition.

Step 3:

An acid / base reaction converts the oxonium into the alcohol.

