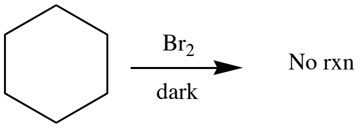
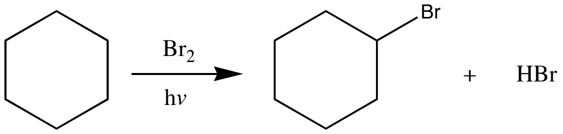
Review of Reactions

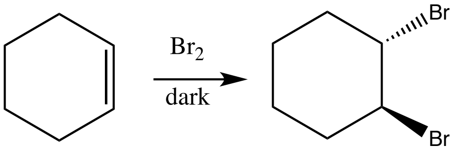
(Note: Reaction will frequently be abbreviated as “rxn” in this course)

Substitution:

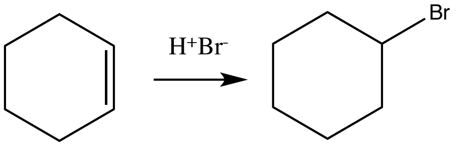




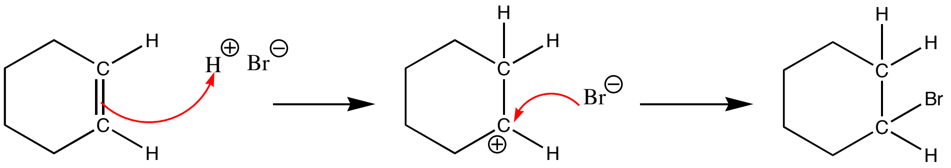
Addition:



fast



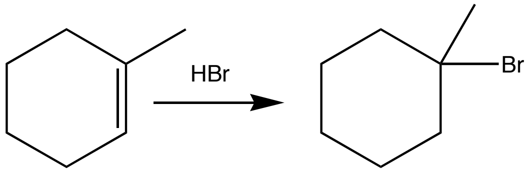
Mechanism:



Carbocation intermediate

Not conjugated cation

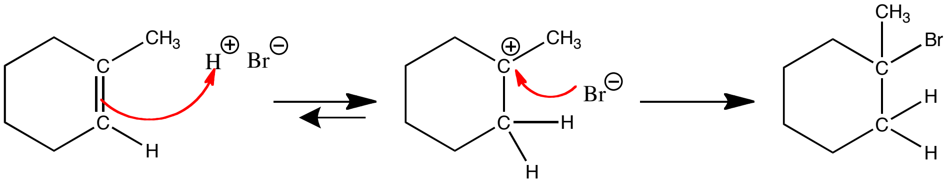
An example of a reaction following the **Markovnikov Rule**:



1-methylcyclohexene

- Positive end adds to least substituted side
- Most stable carbocation intermediate (tertiary)

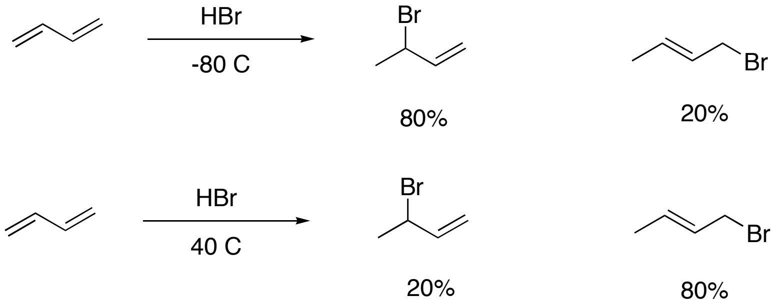
Inductive Effect: Donation (or withdrawal) of electron density through single bonds



the 3^{o} carbocation is the most stable, it has more groups stabilizing the postive charge

cation (and radical) stability: $3^{o} > 2^{o} > 1^{o}$
allylic cation $> 3^{o} > 2^{o} > 1^{o}$

Addition Reactions of Conjugated Systems

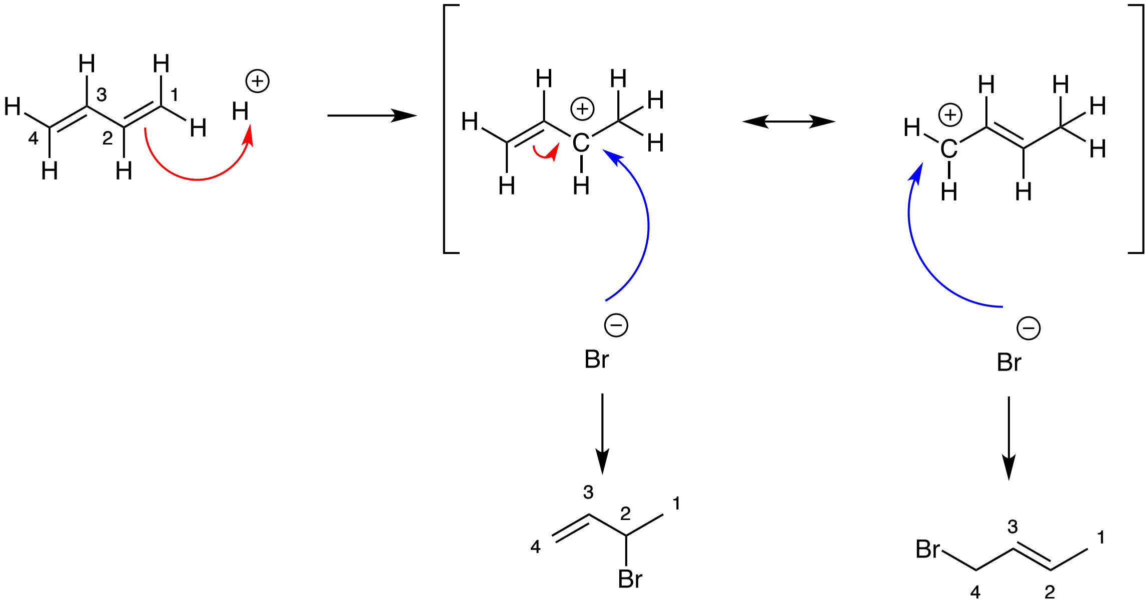


1,3-butadiene 3-bromo-1-butene 1-bromo-2-butene

These are structural isomers.

The product 3-bromobutene is a **1,2-addition** product, whereas 1-bromo-2-butene is the product of an **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene.

Why does the temperature affect the ratio obtained?



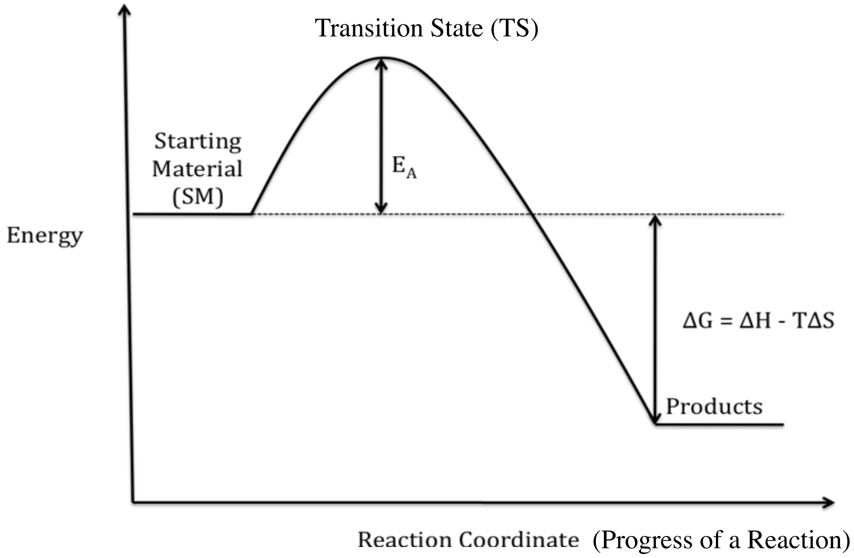
From the 2 resonance forms (connected by the double-headed arrow) of the allylic cation in the above figure, we see that the positive charge is shared between the C2 and C4.

Note: The allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

***Answer to the above question*:**

- 3-bromo-1-butene has a higher yield at the lower temperature because it is formed faster than 1-bromo-2-butene: **kinetic control**
- 3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation, and then form 1-bromo-2-butene which is the thermodynamically more favoured product.

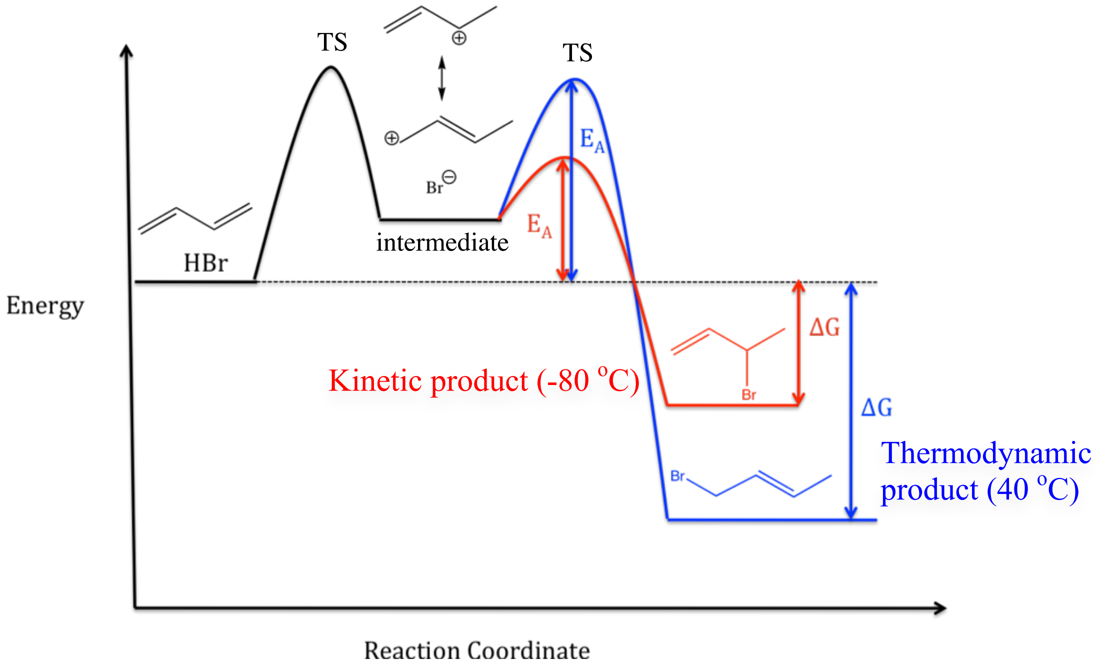
To understand thermodynamic and kinetic control, let's look at the reaction's energy diagram.



ΔG = Free energy of the reaction – this determines ratio of starting material and product
ΔH = Enthalpy of the reaction (change in bond energies)
T = Temperature (in degrees Kelvin)
ΔS = Entropy (a measure of disorder)
E_A = Activation energy (the amount of energy needed for reaction to proceed). This is a factor that determines the rate of a reaction. When E_A is small the reaction is fast; when it is large the reaction is slow.
Transition State (TS) = Where bonds are partially made and partially broken

For an exothermic reaction, there is release of heat and ΔG is always negative (depicted in the energy diagram, the product would be lower on the energy diagram than the starting material).

Now let's look at the energy diagram of the HBr addition to butadiene reaction

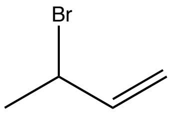


The activation energy barrier to form the 1,2-product, 3-bromo-1-butene is much *smaller* than the 1,4-product, 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically favoured**).

However, the energy of 1-bromo-2-butene is lower than 3-bromo-1-butene, so that it is more **stable** than 3-bromo-1-butene (it is **thermodynamically favoured**).

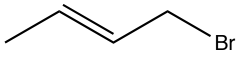
Why is 1-bromo-2-butene more stable?

- The bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes.
- Alkene carbons are somewhat electron deficient. More highly substituted alkenes are more stable due to donation of electron density by the substituents (C vs H)



1,2-addition

monosubstituted C=C

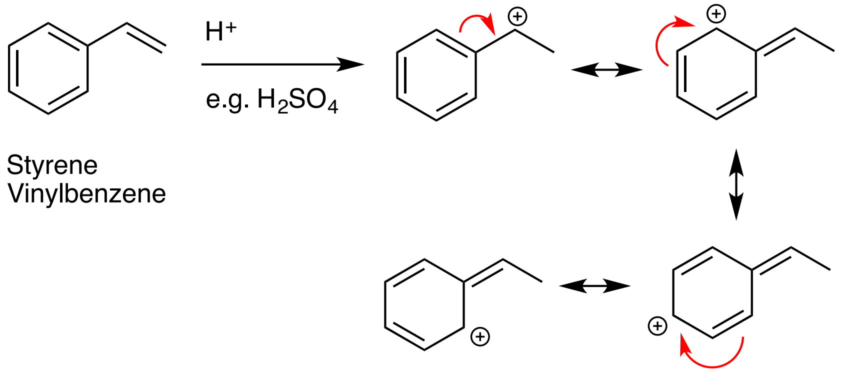


1,4-addition

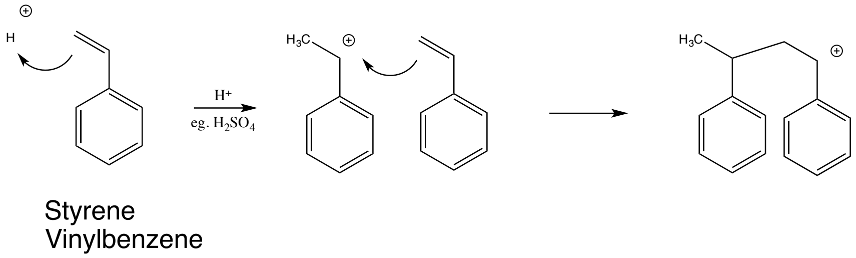
disubstituted C=C

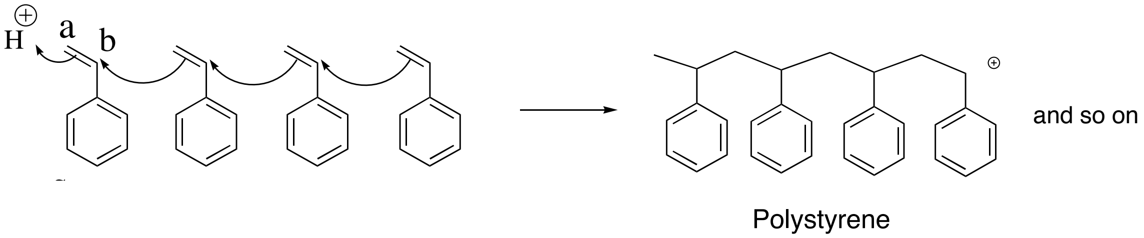
Practical Applications for Conjugated Addition Reactions:

Example: Polystyrene formation by conjugated cation process

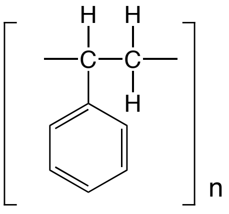


Highly resonance-stabilized carbocation formed from addition of H to the end carbon. Reaction typically takes place on the side chain, keeping the aromatic benzene system intact.





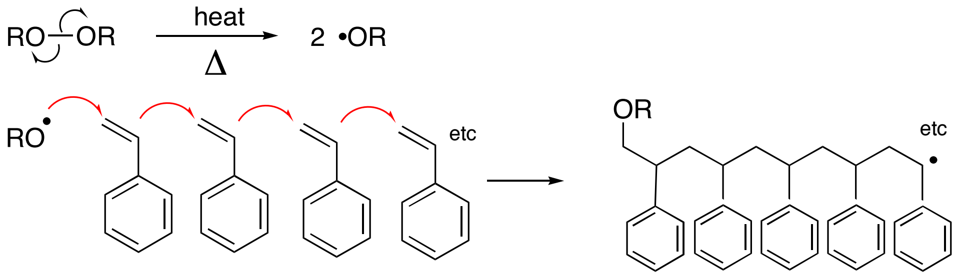
Drawing convention for polymers



Polystyrene n = number of repeating units

Example: Polystyrene formation via a conjugated radical mechanism

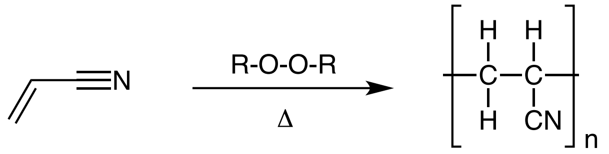
When peroxides are heated, peroxy radicals can be formed:



Growing polystyrene

The peroxy radical can add onto the double bond, forming a carbon-based radical. The radical formed is more stable in the benzylic position adjacent to the phenyl ring. This radical can then add onto another molecule of styrene, and this repeats to form a polymer.

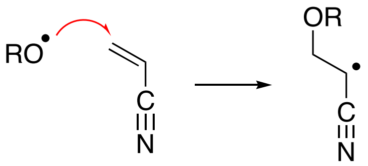
Example: Polyacrylonitrile (Orlon) synthesis (by a conjugated radical process)



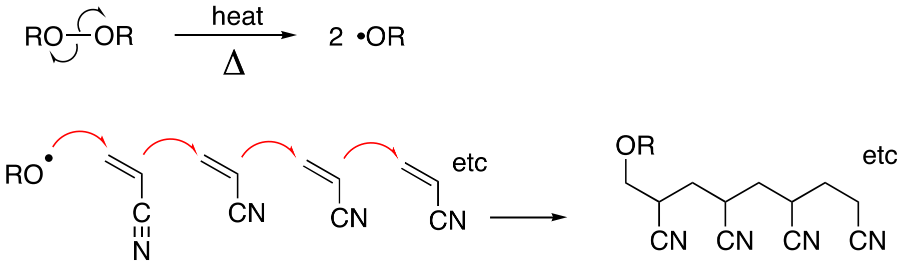
acrylonitrile
(monomer)

polyacrylonitrile
Orlon

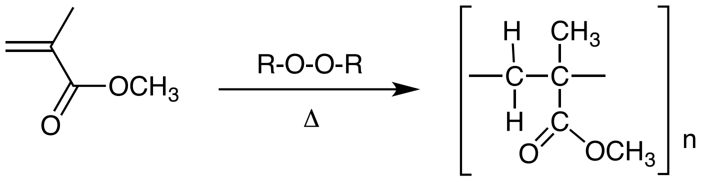
This example is similar to the radical mechanism of polystyrene formation



The radical formed on the carbon is stabilized by the adjacent cyano group



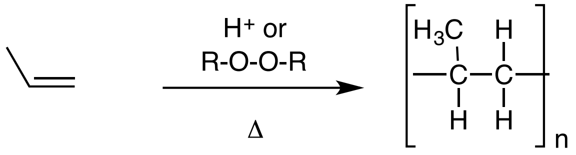
More radical polymerizations:



methylmethacrylate

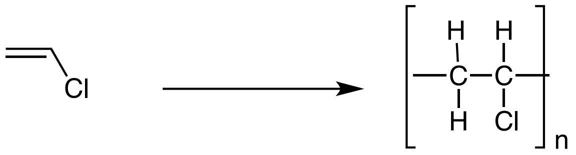
polymethylmethacrylate
Leucite

Leucite = Plexiglass (car windshields, some kitchen utensils, some glass panels)



propene

polypropylene



vinyl chloride

polyvinyl chloride
PVC