Polystyrene



Example: Mechanism of polystyrene formation



Short-hand for mechanism of polystyrene formation





Divinyl benzene can be added as a cross-linker so chains link on both of its double bonds This make the copolymer more solid (as you encounter in many products) – typically about one part in 100 to one part in 6 of divinylbenzene may be added



Conjugated Systems

Definition: Systems that are separated by exactly one single bond from a double bond

Compounds containing conjugated systems:

Polyenes:

Example: **1,3-Butadiene**

Double bonds are separated by one single bond: conjugated

Example: allene (not conjugated_

H₂C=C=CH₂ not conjugated

Example: 1,4-pentadiene (not conjugated)







1,3-pentadiene is planar often so that p-orbitals can overlap as seen below. The partial interaction of orbitals in the middle bond shortens the bond length due to partial double bond character. There is still rapid rotation about the single bond between the two double

bonds, but the preferred conformation all pi bonds aligned. (Transoid preferred over ciosoid)



1,3-Pentadiene prefers to be planar so that p-orbitals can overlap

Absorption of radiation

Molecular Orbitals:

Example 1: Ethylene



Looking at both sigma and pi bonds



Looking only at the π orbitals:



An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). The electron can go back to it's original orbital and heat (or light) is produced in the process. Now for a conjugated system, 1,3-butadiene





As the # of double bonds in the compound increases, decreasing the HUMO-LUMO gap, the energy of the light needed to excite the compound to its excited state is lower.

Once the absorption of light leaves the UV range and into the visible range, the transition becomes visible and the colour of the compound can be seen.



Retinal is combined with the protein opsin in the eye to make rhodopsin, which is a key protein in the mechanism of sight.

Human vision covers the range of 400 nm (4000 Å) to 800 nm (8000 Å), anything outside of these wavelengths is invisible to the naked eye.

The further oxidized form of retinal is retinoic acid. Changing the double bond bearing the carboxylic acid from trans to cis gives the drug Accutane, used to treat acne. (can cause birth defects = teratogen)

diastereomers





Retinoic acid

Accutane

Light Emission : NOT DISCUSSED in Class - for reference only



Another diagram (from Wikipedia) depicting the same idea with additional vibrational energy states is shown below



Many commercial clothes detergents contain fluorescent dyes. These absorb in UV and emit in blue, thereby making colours appear brighter and whites appear white. Some are anthrone / anthrol or derivatives. The two compounds are tautomers (rapidly interconverting structural isomers)



The two possible products are structural isomers.

The product 3-bromobutene is a **1,2-addition** product, whereas 1-bromo-2-butene is the product of a **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.

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*. Neither resonance form depicts the actual structure, but rather the molecule exists as a combination of the two resonance forms. The 'primary carbocation' is stabilized, as it is allylic.

Why does the temperature affect the ratio obtained?

- 3-bromo-1-butene has a higher yield at the lower temperature because it is formed faster than 1-bromo-2-butene due to it's lower E_a: 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 as it is more stable. The thermodynamic product is determined by the equilibrium result controlled by ΔG .

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



Reaction Coordinate

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 1,2-product **kinetically favored**).

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 (the 1,4-product is **thermodynamically favored**).

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)

Br

1,2-addition

monosubstituted C=C

Br disubstituted C=C 1,4-addition