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



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Conjugated Systems

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

Compounds containing conjugated systems:

Polyenes:

Example 1: 1,3-butadiene



Double bonds are separated by one single bond

Tends to be planar; p orbitals want to be aligned, even though rotation along the sigma bond is not restricted. Transoid conformation is in equilibrium with cisoid conformation.







Examples: Conjugated or Not?









Conjugated (relatively unreactive)



Example of conjugated and not conjugated system:



Electromagnetic Spectrum:

1nm = 10 angstrom



UV and visible light: conjugated double bond systems absorb UV light and some visible light



Molecular Orbitals:

Example 1: Ethylene



Looking both at sigma and pi orbitals:



A.O. means atomic orbitals (s, sp², p) M.O. means molecular orbitals (σ , π)

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 its original orbital and heat (or light) is produced in the process. When the electron is promoted to a higher energy state (excited to a higher energy molecular orbital), it attains a **singlet state**. The electron can go back to its original orbital and heat (or light) is produced in the process.



Node: a point or plane of zero electron density in an orbital **HOMO**: Highest Occupied Molecular Orbital **LUMO**: Lowest Unoccupied Molecular Orbital



As the number 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 color of the compound can be seen.

Example 3: 1,3,5,7,9,11-dodecahexaene



Conjugated molecules in vision:



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)

OH

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Retinoic acid

Accutane



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

<u>Thermodynamic vs. Kinetic Products: Reaction of Dienes -</u> This part and following eligible for Exam



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.

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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 its 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 **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 (it is **thermodynamically favored**).

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Kinetic control: governed by the activation energy (Ea) **Thermodynamic control:** you get an equilibrium mixture. Governed by ΔG .

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)



Polymerization: If no nucleophile is present in previous addition reaction - e.g. isoprene



Rubber tree (Hivea brasiliensis) produces approximately 2000-4000 lbs/acre of rubber.