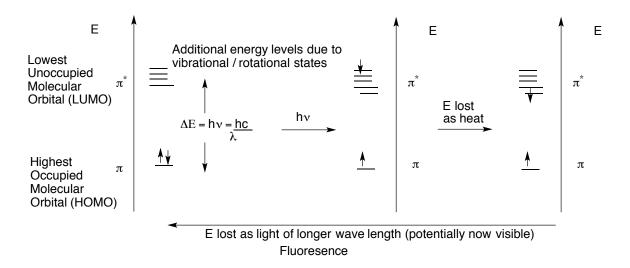
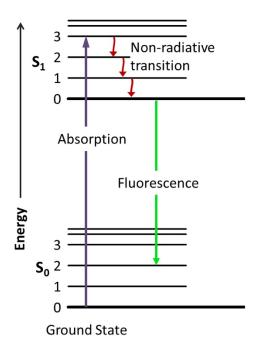
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<u>Light Emission -NOT COVERED IN CLASS</u> <u>THIS PART FOR REFERENCE</u> ONLY - NOT ON EXAM

- 1) Fluorescence
- Absorb UV and emit either UV or Visible
- Short life (singlet state electrons paired)
- 2) Phosphorescence
- Absorb UV and emit Visible
- Long life (triplet state electrons not paired)
- 3) Chemiluminescence
- Reactions that produce light



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)

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

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.

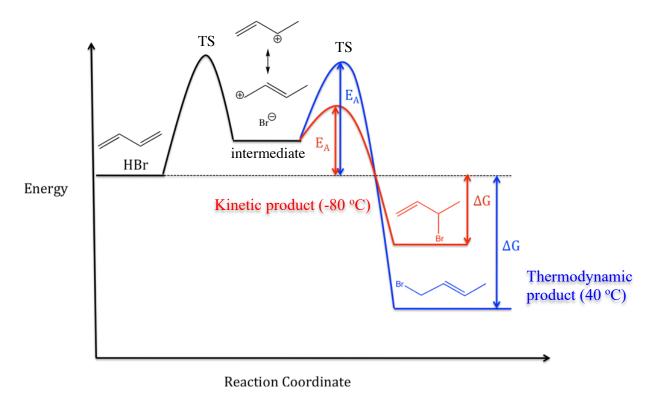
Note: The allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a *single entity*. Neither resonance form depicts the actual structure, but rather the molecule exists as a combination of the two resonance forms. The 'primary carbocation' 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 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

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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**).

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.

Alcohol and Ether Nomenclature

Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of organic groups bonded to the hydroxyl bearing carbon.

Note: -OH is called hydroxyl, hydroxy or alcohol

Naming:

- 1. Find the longest chain, with the maximum number of OH groups.
- 2. Number in such a way to give the **first OH** the lowest number
- 3. Drop the "e" of the alkane name, add "ol"

Note: the alcohol (-OH) takes priority over ethers, multiple bonds, and halogens

Examples:

Eicosa-6Z,9Z,12Z,15Z-tetraen-1-ol

Note: most alcohols are flammable, however, as the chain gets longer, the molecules would tend to stick together (i.e., intermolecular forces) and would be less flammable.

Steroids

Steroid Skeleton

Characterized by a methyl group in C13

Types of Steroids

Estrone

Androstane

Characterized by the presence of -CH $_{\rm 3}$ groups in C10 and C13

Estradiol

Testosterone

Androsterone

Pregnane

- Characterized by two -CH₃ groups in C10 and C13, and a substituent in C17
- Not biologically active

ProgesteronePregnancy Hormone

Cortisone

(Adrenocorticoid)
Characterized by a carbonyl at C11 and pregnane skeleton

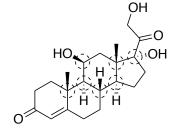
Cortisol Stress Hormone

Cholestane

Cholesterol

Estradiol -Female sex hormone

Testosterone -Male sex hormone



Cortisol -Stress hormone

Stereogenic centers