Addition Reactions of Comjugated Systems

Thermodynamic vs. kinetic products



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 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).

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 Br monosubstituted C=C disubstituted C=C 1,4-addition

1,2-addition



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

Vulcanized Rubber Elastic