TRU Open Press

Alkene and Diene Stability

Transcript

Instructor: Jessie Key

00:00:00:00 - 00:00:30:30
Instructor: Logan, Doctor Jessie Key here, in this video, we'll explore the relative stability of alkenes and dienes and use molecular orbital theory to help us explain the stability of conjugated dienes. Remember that generally, trans alkenes are more stable than cis alkenes. This can be rationalized by the steric strain penalty that cis alkenes face, which can be visualized when looking at the space filling diagrams of Cis and trans but-2-ene.

00:00:30:30 - 00:00:52:22
Instructor: In the space filling diagram, the carbon atoms are shown in this dark gray or black color, and the hydrogens in white. Notice on the right side of the slide that the methyl hydrogens in Cis but-2-ene are physically too close together, resulting in the steric strain. Hyperconjugation is an important stabilizing effect seen with alkenes.

00:00:52:22 - 00:01:48:41
Instructor: The more substituted in alkene, the more electron density that can delocalize to the SP two hybridized carbons of the Pi bond. We see this reflected in the general trend for alkene stability, where disubstituted alkenes are more stable than monosubstituted, tri substituted, more stable than disubstituted, and tetrasubstituted the most stable. So if we combine the steric factor, cis versus trans discussed on the previous slide with the electronic factor discussed on this slide, we can make a more inclusive order of alkene stability with monosubstituted being the least stable, cis disubstituted being more stable, geminal and trans die substitute being roughly equal and more stable than cis, trisubstituted being more stable than disubstituted, and finally tetrasubstituted being the most stable.

00:01:48:41 - 00:02:11:49
Instructor: Conjugation is an effect that can help stabilize the diene or polyene. Conjugate dienes exhibit greater stability than isolated alkenes, which can be demonstrated by their heats of hydrogenation. For Ba 13 diene, there is an observed stabilization energy of about 15 kilojoules per mole, which arises from the increased stability from delocalization of pi electrons throughout the entire molecule.

00:02:11:49 - 00:02:50:88
Instructor: This can be observed in the form of partial double bond character that exists in the carbon two carbon three bond, which is evidenced in both the shorter bond length of 148 picometres compared to a typical 153 Picometers and also in the electrostatic potential map

diagram below, areas of high electron density are shown with brighter orange and red colors, while areas that are electron poor are shown with blue and green colors. As you can see, there's significant sharing of electron density across the entire carbon backbone indicating delocalization. Molecular orbital theory can help us explain why we see this partial double bond character between carbons two and three.

00:02:50:88 - 00:03:16:35
Instructor: Let's quickly refresh ourselves on MO theory. In molecular orbital theory, we are mathematically combining atomic orbitals to generate new orbitals that span the entirety of the molecule known as molecular orbitals. In the molecular orbital diagram of hydrogen H two shown, we are combining the two IS orbitals of each hydrogen atom to generate two new molecular orbitals for the molecule H two.

00:03:16:72 - 00:03:49:12
Instructor: A lower energy bonding molecular orbital is generated by constructive interference, and a higher energy antibonding molecular orbital is generated by destructive interference. The two electrons fill the molecular orbitals from the bottom up following the off-bow principle to give us a filled bonding molecular orbital and an unfilled antibonding molecular orbital. Notice the lower energy bonding molecular orbital contains no nodes, while the antibonding molecular orbital is composed of two phases separated by a node.

00:03:49:12 - 00:04:07:10
Instructor: A node is an area of zero electron density that is always a destabilizing feature. The more nodes in a molecular orbital, the higher the energy. We can similarly combine P orbitals to generate a lower energy P bonding molecular orbital and a P anti bonding molecular orbital.

00:04:07:10 - 00:04:46:51
Instructor: A conjugate dine zeta 13 dine is comprised of four overlapping P orbitals which mathematically combine to give four new molecular orbitals, C one, C two, C three star, and Si four star. The two lower energy molecular orbitals, S one and S two correspond to bonding molecular orbitals, while the two higher energy molecular orbitals, C three star and s four star are anti bonding as denoted by the star in their names. The four electrons of the system fill the two lower energy bonding molecular orbitals, s one and s two, and we can turn our focus to those.

00:04:46:51 - 00:05:13:15
Instructor: In s one, there's continuous overlap between all of the carbons, indicating double bond character present between all carbons, including carbon two and carbon three. However, in s two, there's a node present between carbons two and three, indicating a lack of double bond character. This explains the partial double bond character present between carbons two and three, since there is double bond character in one of the filled bonding molecular orbitals and not the other.

00:05:14:14 - 00:05:35:00
Instructor: Two conformers are possible for Ba 13 diene, which exhibit conjugation, SCIs and S trans. This nomenclature denotes the arrangement of the two alkene groups relative to their connecting Sigma bond. Both of these conformations allow for continuous conjugation of the Pi system.

00:05:35:00 - 00:05:54:37
Instructor: However, the S trans conformation is greatly favored. At room temperature, there's

an equilibrium between the two conformers, but 98% of the molecules will adopt the S trans conformation at any given time. This diagram, we have free energy on the y axis and dihedral angle on the X axis.

00:05:54:37 - 00:06:29:83
Instructor: As we go from the SCIs to the S trans conformation, at the 90 degree dihedral angle, the two Pi bonds are no longer able to overlap, and it represents an energy maximum where there is no stabilization from conjugation. As the dihedral angle increases to 180 degrees, the S trans conformation is achieved, and we see a 12 kilojoules per mole decrease in energy due to the reduced steric penalty from being arranged trans. This explains the 98 to two preference for adoption of the S trans conformation.