Alkene and Diene Stability

Transcript

00:00:00:00 - 00:00:12:60

Dr.Jessie Key: Hello again, Dr. Jessie Key here. In this video, we will explore the relative stability of alkenes and dienes and use molecular orbital theory to help us explain the stability of conjugated dienes.

00:00:12:60 - 00:00:38:24

Dr.Jessie Key: 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. In the space filling diagram, the carbon atoms are shown in this dark gray or black color, and the hydrogens in white.

00:00:38:24 - 00:01:00:02

Dr.Jessie Key: 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. The more substituted in alkene, the more electron density that can delocalize to the sp2 hybridized carbons of the pi bond.

00:01:00:02 - 00:01:53:33

Dr.Jessie Key: We see this reflected in the general trend for alkene stability, where disubstituted alkenes are more stable than monosubstituted, trisubstituted, more stable than disubstituted, and tetrasubstituted the most stable. So if we combine the steric factor, cis vs 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 monosubstitute being the least stable, cis disubstituted being more stable, geminal and trans disubstitute being roughly equal and more stable than cis, trisubstitute being more stable than disubstituted, and finally tetrasubstitute being the most stable. Conjugation is an effect that can help stabilize the diene or polyene.

00:01:53:33 - 00:02:35:96

Dr.Jessie Key: Conjugate dienes exhibit greater stability than isolated alkenes, which can be demonstrated by their heats of hydrogenation. For buta-1,3-diene, there is an observed stabilization energy of about 15 kJ/mol, which arises from the increased stability from delocalization of pi electrons throughout the entire molecule. This can be observed in the form of partial double bond character that exists in the carbon two carbon three (C2-C3) bond, which is evidenced in both the shorter bond length of 148 picometers compared to a typical 153 picometers and also in the electrostag 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.

00:02:35:96 - 00:02:54:73
Dr.Jessie Key: As you can see, there's significant sharing of electron density across the entire carbon backbone indicating delocalization. Molecular orbital theory (MO theory) can help us explain why we see this partial double bond character between carbons 2 and 3. Let's quickly refresh ourselves on MO theory.

00:02:54:73 - 00:03:27:84
Dr.Jessie Key: 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, H2, shown, we are combining the two 1s orbitals of each hydrogen atom to generate two new molecular orbitals for the molecule H2. A lower energy bonding molecular orbital is generated by constructive interference, and a higher energy antibonding molecular orbital is generated by destructive interference.

00:03:27:84 - 00:03:54:88
Dr.Jessie Key: The two electrons fill the molecular orbitals from the bottom up following the Aufbau 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. A node is an area of zero electron density that is always a destabilizing feature.

00:03:54:88 - 00:04:20:98
Dr.Jessie Key: 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 antibonding molecular orbital. A conjugate diene buta-1,3-diene is comprised of four overlapping p orbitals which mathematically combine to give four new molecular orbitals, psi1, psi2, psi3 star and psi4 star.

00:04:21:11 - 00:04:56:29
Dr.Jessie Key: The two lower energy molecular orbitals, psi1 and psi2 correspond to bonding molecular orbitals, while the two higher energy molecular orbitals, psi3 star and psi4 star, are antibonding as denoted by the star in their names. The four electrons of the system fill the two lower energy bonding molecular orbitals, psi1 and psi2, and we can turn our focus to those. In psi1, there's continuous overlap between all of the carbons, indicating double bond character present between all carbons, including carbon two and carbon three (C2 and C3).

00:04:56:29 - 00:05:23:06
Dr.Jessie Key: However, in psi2, there's a node present between carbons 2 and 3, 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. Two conformers are possible for buta-1,3-diene which exhibit conjugation, s-cis and s-trans.

00:05:23:30 - 00:05:38:48
Dr.Jessie Key: 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. However, the s-trans conformation is greatly favored.

00:05:38:48 - 00:06:08:51
Dr.Jessie Key: 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. In this diagram, we have free energy on the y-axis and dihedral angle on the x-axis. As we go from the s-cis 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.

00:06:08:63 - 00:06:29:83
Dr.Jessie Key: As the dihedral angle increases to 180 degrees, the s-trans conformation is achieved, and we see a 12 kJ/mol decrease in energy due to the reduced steric penalty from being arranged trans. This explains the 98 to 2 preference for adoption of the s-trans conformation.