

## 7.7: STABILITY OF ALKENES

### OBJECTIVES

After completing this section, you should be able to

- explain why *cis* alkenes are generally less stable than their *trans* isomers.
- explain that catalytic reduction of a *cis* alkene produces the same alkane as the catalytic reduction of the *trans* isomer.
- explain how heats of hydrogenation ( $\Delta H^\circ_{\text{hydrog}}$ ) can be used to show that *cis* alkenes are less stable than their *trans* isomers, and discuss, briefly, the limitations of this approach.
- arrange a series of alkenes in order of increasing or decreasing stability.
- describe, briefly, two of the hypotheses proposed to explain why alkene stability increases with increased substitution. [Note: This problem is a typical example of those instances in science where there is probably no single “correct” explanation for an observed phenomenon.]

### KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- catalytic hydrogenation
- heat of hydrogenation ( $\Delta H^\circ_{\text{hydrog}}$ )
- hyperconjugation

### STUDY NOTES

The two alkenes, *cis*-CH<sub>3</sub>CH=CHCH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> have similar heats of hydrogenation (−120 kJ/mol and −119 kJ/mol, respectively), and are therefore of similar stability. However, they are both less stable than *trans*-CH<sub>3</sub>CH=CHCH<sub>3</sub> (−116 kJ/mol).

You may wonder why an *sp*<sup>2</sup>-*sp*<sup>3</sup> bond is stronger than an *sp*<sup>3</sup>-*sp*<sup>3</sup> bond. Bond strength depends on the efficiency with which orbitals can overlap. In general, *s* orbitals overlap more efficiently than do *p* orbitals; therefore, the *s-s* bond in the hydrogen molecule is stronger than the *p-p* bond in fluorine. In hybrid orbitals, the greater the *s* character of the orbital, the more efficiently it can overlap: an *sp*<sup>2</sup> orbital, which has a 33% *s* character, can overlap more effectively than an *sp*<sup>3</sup> orbital, with only 25% *s* character.

## HYDROGENATION

Alkene hydrogenation is the addition of hydrogen gas (H<sub>2</sub>) to an alkene which saturates the bond and forms an alkane. Alkene hydrogenation reactions require a transition metal catalyst, such as Pt or Pd, to speed up the reaction. The hydrogenation reaction is used in this section to investigate the stability of alkenes, however, it will be discussed in greater detail in **Section 8.7**. Hydrogenation reactions are exothermic and the enthalpy change in this reaction is called the heat of hydrogenation ( $\Delta H^\circ_{\text{hydrog}}$ ). Since the double bond is breaking in this reaction, the energy released during hydrogenation is proportional to the energy in the double bond of the molecule. By comparing the heat of hydrogenations from a series of alkenes that produce the same alkane, a quantitative measure of relative alkene stabilities can be produced. These experiments will lead to an general understanding of structural features which tend to stabilize or destabilize alkenes.

## THE CATALYST

A **catalyst** increases the reaction rate by lowering the activation energy of the reaction. Although the catalyst is not consumed in the reaction, it is required to accelerate the reaction sufficiently to be observed in a reasonable amount of time. Catalysts commonly used in alkene hydrogenation are: platinum, palladium, and nickel. The metal catalyst acts as a surface on which the reaction takes place. This increases the rate by putting the reactants in close proximity to each other, facilitating interactions between them. With this catalyst present, the sigma bond of H<sub>2</sub> breaks, and the two hydrogen atoms instead bind to the metal (see #2 in the figure below). The  $\pi$  bond of the alkene weakens as it also interacts with the metal (see #3 below).

Since both the reactants are bound to the metal catalyst, the hydrogen atoms can easily add, one at a time, to the previously double-bonded carbons (see #4 and #5 below). The position of both of the reactants bound to the catalyst makes it so the hydrogen atoms are only exposed to one side of the alkene. This explains why the hydrogen atoms add to same side of the molecule, called *syn*-addition.

 NOTE

## HEATS OF HYDROGENATION

Diagram illustrating the stability of alkenes based on substitution:

Top row (Stability): least stable (higher  $\Delta H^\circ$ ) on the left, most stable (lower  $\Delta H^\circ$ ) on the right.

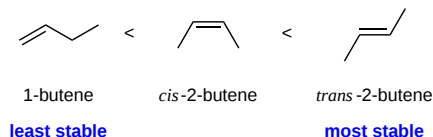
Bottom row (Substitution): least substituted on the left, most substituted on the right.

Alkenes shown from left to right:

- not substituted (ethene): H2C=CH2
- monosubstituted alkene: H2C=CH-R
- cis-disubstituted alkene: R1CH=CHR2 (cis)
- trans-disubstituted alkene: R1CH=CHR2 (trans)
- trisubstituted alkene: R12C=CHR3
- tetrasubstituted alkene: R1R2C=CR3R4

Stability increases from left to right: not substituted < monosubstituted < cis-disubstituted < trans-disubstituted < trisubstituted < tetrasubstituted.

See the following isomers of butene:



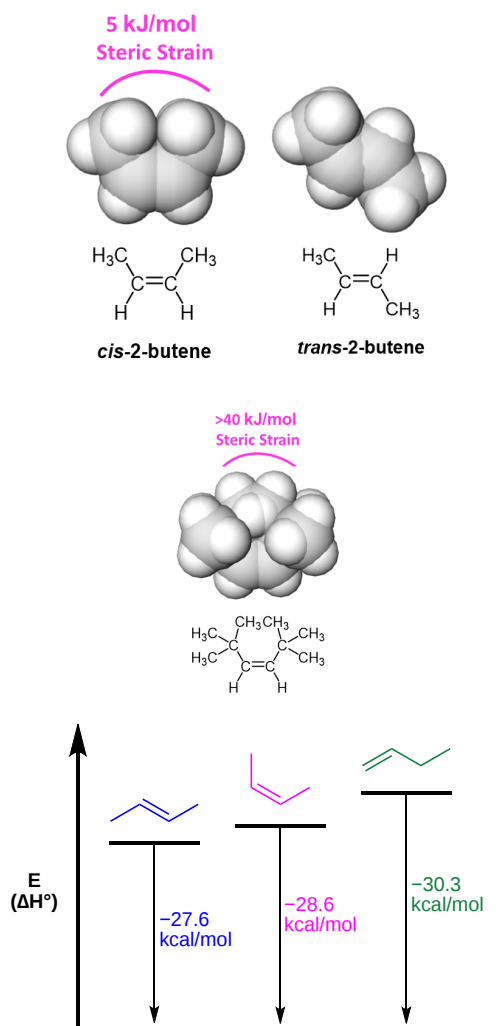


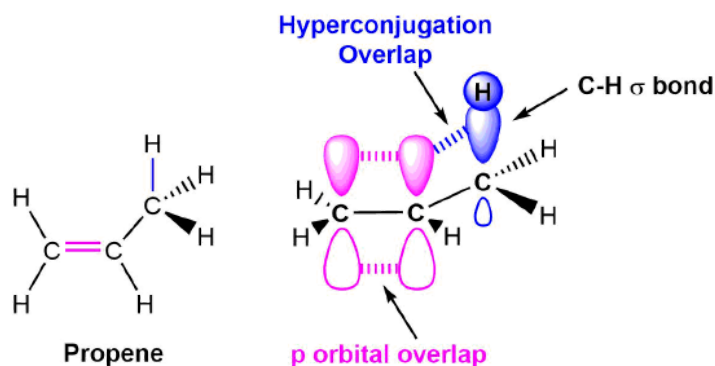
Figure 7.7.2: *Trans*-2-butene is the most stable because it has the lowest heat of hydrogenation.

## ALKENE STABILIZATION BY ALKYL SUBSTITUENTS

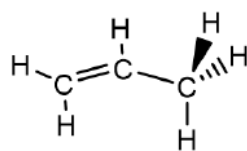
In general, the stability of an alkene increases with the number of alkyl substituents. This effect is due by the combination of two factors:

### HYPERCONJUGATION

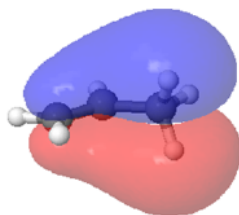
In classical valence-bond theory, electron delocalization can only occur by the parallel overlap of adjacent p orbitals. According to hyperconjugation theory, electron delocalization could also occur by the parallel overlap of p orbitals with adjacent hybridized orbitals participating in sigma bonds. This electron delocalization serves to stabilize the alkene. As the number of alkyl substituents increases, the number of sigma bonds available for hyperconjugation increases, and the alkene tends to become more stabilized. In the example of propene shown below, a p orbital from a  $sp^2$  hybridized carbon involved in the double bond interacts with a  $sp^3$  hybridized orbital participating in an adjacent C-H sigma bond.



In a molecular orbital description of hyperconjugation, the electrons in sigma molecular orbitals (C-H or C-C) of alkyl substituents, interact with adjacent unpopulated non-bonding or antibonding molecular orbitals from the double bond. The interaction creates a bonding molecular orbital which extends over the four atom chain (C=C-C-H) involved in hyperconjugation. The expanded molecular orbital helps to stabilize the double bond.



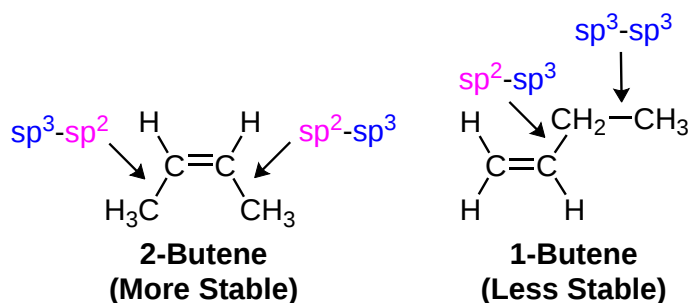
Propene



Extended Bonding MO  
created by hyperconjugation

### BOND STABILITY

Bond strengths play an important part in determining the overall stability of a molecule. A C-C bond between a  $sp^3$  carbon and a  $sp^2$  carbon is slightly stronger than a C-C bond between two  $sp^3$  carbons. Increasing the number alkyl substituents of a double bond also increases the number of  $sp^3$ - $sp^2$  C-C bonds making the alkene more stable. This idea can be clearly seen when comparing the isomers 1-butene and 2-butene. The molecule 1-butene is monosubstituted and contains a  $sp^3$ - $sp^3$  C-C and a  $sp^3$ - $sp^2$  C-C bond. The disubstituted, 2-butene, contains 2  $sp^3$ - $sp^2$  C-C bonds which contributes to its greater stability.



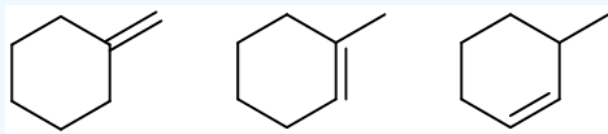
#### NOTE

In cycloalkenes smaller than cyclooctene, the cis isomers are more stable than the trans as a result of ring strain.

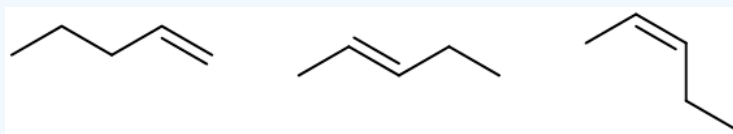
#### EXERCISE 7.7.1

Of the three following isomers which would be expected to be the most stable?

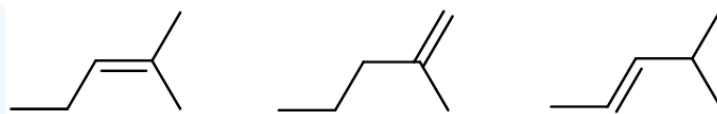
a)



b)



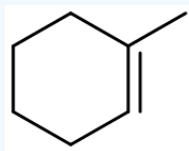
c)



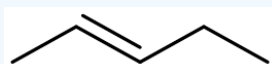
Answer

1)

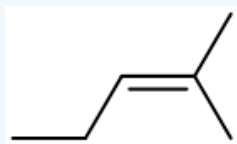
a)



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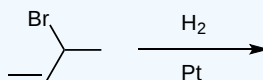


c)



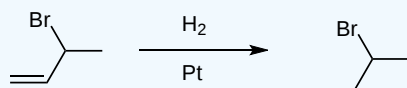
### ? EXERCISE 7.7.2

3-Bromobut-1-ene reacts with hydrogen gas in the presence of a platinum catalyst. What is the name of the product?



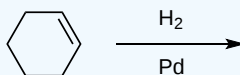
Answer

2-Bromobutane (numbering changes when alkene is no longer present)



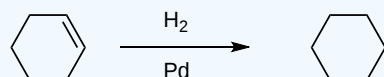
### ? EXERCISE 7.7.3

Cyclohexene reacts with hydrogen gas in the presence of a palladium catalyst. What is the name of the product?



Answer

Cyclohexane



### ? EXERCISE 7.7.4

What is the stereochemistry (syn or anti addition) of an alkene hydrogenation reaction?

**Answer**

Syn-addition

### ? EXERCISE 7.7.5

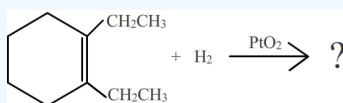
When looking at their heats of hydrogenation, is the cis or the trans isomer generally more stable?

**Answer**

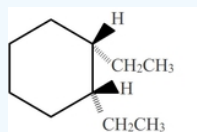
Trans

### ? EXERCISE 7.7.6

Show the product for the following



**Answer**



## REFERENCES

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5. Zlatkis, Albert, Eberhard Breitmaier, and Gunther Jung. A Concise Introduction to Organic Chemistry. New York: McGraw-Hill Book Company, 1973.

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