

radicals, each of which then loses a hydrogen atom to generate two molecules of ethylene.



Steam cracking is an example of a reaction whose energetics are dominated by entropy ( $\Delta S^\circ$ ) rather than by enthalpy ( $\Delta H^\circ$ ) in the free-energy equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . Although the bond dissociation energy  $D$  for a carbon-carbon single bond is relatively high (about 370 kJ/mol) and cracking is endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the high temperature, makes the  $T\Delta S^\circ$  term larger than the  $\Delta H^\circ$  term, thereby favoring the cracking reaction.

## 7.2 Calculating Degree of Unsaturation

Because of its double bond, an alkene has fewer hydrogens than an alkane with the same number of carbons— $C_nH_{2n}$  for an alkene versus  $C_nH_{2n+2}$  for an alkane—and is therefore referred to as **unsaturated**. Ethylene, for example, has the formula  $C_2H_4$ , whereas ethane has the formula  $C_2H_6$ .



**Ethylene:  $C_2H_4$**   
(Fewer hydrogens — Unsaturated)



**Ethane:  $C_2H_6$**   
(More hydrogens — Saturated)

In general, each ring or double bond in a molecule corresponds to a loss of two hydrogens from the alkane formula  $C_nH_{2n+2}$ . Knowing this relationship, it's possible to work backward from a molecular formula to calculate a molecule's **degree of unsaturation**—the number of rings and/or multiple bonds present in the molecule.

Let's assume that we want to find the structure of an unknown hydrocarbon. A molecular weight determination on the unknown yields a value of 82 amu, which corresponds to a molecular formula of  $C_6H_{10}$ . Since the saturated  $C_6$  alkane (hexane) has the formula  $C_6H_{14}$ , the unknown compound has two fewer pairs of hydrogens ( $H_{14} - H_{10} = H_4 = 2 H_2$ ) so its degree of unsaturation is 2. The unknown therefore contains two double bonds, one ring and one double bond, two rings, or one triple bond. There's still a long way to go to establish structure, but the simple calculation has told us a lot about the molecule.



**4-Methyl-1,3-pentadiene**  
(two double bonds)



**Cyclohexene**  
(one ring, one double bond)



**Bicyclo[3.1.0]hexane**  
(two rings)



**4-Methyl-2-pentyne**  
(one triple bond)

$C_6H_{10}$

# Vol 7 Structure And Reactivity

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