

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 (ΔS°) rather than by enthalpy (ΔH°) 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 ΔH° 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 $\text{C}_n\text{H}_{2n+2}$ 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 $\text{C}_n\text{H}_{2n+2}$. 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 ($\text{H}_{14} - \text{H}_{10} = \text{H}_4 = 2 \text{H}_2$) 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}

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D Kirk

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