

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^\ddagger) rather than by enthalpy (ΔH^\ddagger) in the free-energy equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. 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 $T\Delta S^\ddagger$ term larger than the ΔH^\ddagger 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}

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Marek Majewski, Victor Snieckus



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Molecular Simulation on Cementitious Materials: From Computational Chemistry Method to Application

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