2.1: PEARLS OF WISDOM

Learning Objective

- define the terms "sterics" and "electrostatics"

INTRODUCTION

Functional groups are the common bonding patterns found in organic compounds. Organic compounds are classified by their functional groups.

To talk about organic chemistry, we need to be able to

a) recognize and name the major organic functional groups (see chapter 3 for nomenclature)

b) apply bonding theories to the structure of functional groups

c) visual functional groups in three dimensions

d) determine the polarity & intermolecular forces of organic compounds

Ultimately, all of the information above will be integrated at the end of this chapter to predict solubilities and relative boiling points of organic compounds. In future chapters, these skills will help elucidate reaction mechanisms and pathways.

Sterics & Electrostatics - all roads lead to one or other

Sterics and electrostatics are primary considerations when learning the reactions of organic chemistry.

Sterics is the spatial arrangement (3-dimensional structure) of atoms in a molecule or ion.

Electrostatics is the the charge distribution within a molecule or ion.

Depending on the reaction mechanism, either sterics or electrostatics (charge stabilization) will play a dominant role in the rate determining step. For concerted (one-step) reactions, sterics will strongly influence the orientation of reactants in the transition state. For two-step reactions, there is typically a charged intermediate that requires stabilization for the reaction to proceed. The intermediate with the lowest charge distribution is the most stable and reacts preferentially.

Sterics can be predicted using bonding theories. Molecular orbital (MO) theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule. In valence bond theory (VB) theory, atomic orbitals can be hybridized. VB theory assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom. As discussed in chapter 1, this assumption is invalid because some atoms can bond using delocalized electrons through resonance. VB theory does a good job of qualitatively describing the shapes of covalent compounds which is important in determining the sterics of the reactions. While Molecular Orbital (MO) theory is good for understanding bonding in general and the electrostatics of a reactant, intermediate, or product.

Electrostatics are determined by applying the same concepts used to determine the relative acidity of compounds by evaluating the electron density of their conjugate bases. The less charge, the more stable an ion is. The stability of ions is determined by the identity of the element being ionized, charge delocalization via resonance, inductive effects, and orbital hybridization. Inductive effects can be electron withdrawing (aka electronegative) or electron donating, such alkyl group stabilization of carbocations. These parameters are listed in order of importance with the overall character of an ion must be evaluated to determine its relative stability. Refer to section 1.15 of this text for the full explanation.