Chapter 2
Polar Covalent Bonds; Acids and Bases

Bonding in Organic Compds

• Most organic compounds involve bonds between two non-metals
• The bonds can be either polar covalent or non-polar covalent
• Polar covalent occurs between atoms of different electronegativity
• Non-polar covalent occurs between atoms of identical electronegativity
• The greater the electronegativity difference, the greater the polarity

Polar Covalent Bonds

• Covalent bonds can have ionic character
• These are polar covalent bonds
  – Bonding electrons attracted more strongly by one atom than by the other
  – Electron distribution between atoms in not symmetrical
Electronegativity

- **Electronegativity (EN):** intrinsic ability of an atom to attract the shared electrons in a covalent bond
- Differences in EN produce bond polarity
- F is most electronegative (EN = 4.0), Cs is least (EN = 0.7)
- Metals on left side of periodic table attract electrons weakly, lower EN
- Halogens and other reactive nonmetals on right side of periodic table attract electrons strongly, higher electronegativities
- EN of C = 2.5

Inductive Effect

- Nonpolar Covalent Bonds: atoms with similar EN
- Polar Covalent Bonds: Difference in EN of atoms < 2
- Ionic Bonds: Difference in EN > 2
  - C–H bonds, relatively nonpolar C–O, C–X bonds (more electronegative elements) are polar
- Bonding electrons toward electronegative atom
  - C acquires partial positive charge, δ+
  - Electronegative atom acquires partial negative charge, δ−
- **Inductive effect:** shifting of electrons in a bond in response to EN of nearby atoms

Electrostatic Potential Map

- Chlorine: EN = 3.0
- Carbon: EN = 2.5
- Difference = 0.5
**Bond Dipole Moments**

- \( \mu \) (dipole moment, debyes) = \( \delta \) (electric charge) \( \times \) \( d \) (distance)
- Bond dipole moments can range from 0 to 3.6 D, the moment for \( \text{C} \equiv \text{N} \)
- A polar bond is thought of having a partial positive end (\( \delta^+ \)) and a partial negative end (\( \delta^- \))
- The direction of the negative end is shown by:

![Diagram showing bond dipole moments](image)

\( \mu = 0.86 \text{ D} \)
\( \mu = 1.29 \text{ D} \)
\( \mu = 1.51 \text{ D} \)
\( \mu = 1.56 \text{ D} \)
\( \mu = 1.48 \text{ D} \)

**Molecular Dipole Moment**

- Molecules which contain polar covalent bonds may have a net dipole moment
- Each bond is thought of as a vector
- The sum of the vectors reflect the magnitude and direction of the molecular dipole moment

![Diagram showing molecular dipole moments](image)

\( \mu = 1.84 \text{ D} \)
\( \mu = 0 \text{ D} \)
\( \mu = 1.86 \text{ D} \)

**Lone Pairs and Dipole Moment**

- Water, \( \text{H}_2\text{O} \) (\( \mu = 1.85 \text{ D} \))
- Ammonia, \( \text{NH}_3 \) (\( \mu = 1.47 \text{ D} \))
Geometric Isomers

- Isomers are different compounds with the same formula.
- Structural or constitutional isomers differ in how atoms are bonded.
- For example, CH$_3$CH$_2$OH and CH$_3$OCH$_3$ share the same molecular formula, C$_2$H$_6$O, but the atoms are bonded differently.
- Geometric isomers have the same atom connectivity, but have different spatial placement of atoms.

![cis-1,2-dichloroethylene and trans-1,2-dichloroethylene](image)

Problem

Shown below are three isomers of Dichlorobenzene. Which of these would have a nonzero dipole moment?

![Dichlorobenzene isomers](image)

Formal Charge

- Sometimes it is necessary to have structures with formal charges on individual atoms.
- We compare the bonding of the atom in the molecule to the valence electron structure.
- If the atom has one more electron in the molecule, it is shown with a "-" charge.
- If the atom has one less electron, it is shown with a "+" charge.
- Neutral molecules with both a "-" and a "+" are dipolar.
Formal Charge

\[
\text{Formal charge} = \frac{\text{Number of valence electrons in free atom}}{2} - \frac{\text{Number of bonding electrons}}{2}
\]

For the nitromethane structure:

\[
\text{N} : \text{O} \quad \text{H}_2\text{CNN} \quad \text{N} : \text{O} \quad \text{H}_2\text{CNN}
\]

\[
\text{Formal charge} = 3 - 1 = 2
\]

For the cycloglycine nitromethane structure:

\[
\text{O} : \text{O} \quad \text{H}_2\text{CNN} \quad \text{N} : \text{N} \quad \text{H}_2\text{CNN}
\]

\[
\text{Formal charge} = 6 - 4 = 2
\]

Problem

Calculate the formal charges of the atoms shown in red.

Resonance

- Some molecules have structures that cannot be shown with a single representation
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pair(s)
- Such a structure is delocalized and is represented by resonance forms
- The resonance forms are connected by a double-headed arrow
Resonance Hybrid

- A structure with resonance forms does not alternate between the forms
- Instead, it is a hybrid of the two resonance forms, so the structure is called a resonance hybrid
- For example, benzene (C₆H₆) has two resonance forms with alternating double and single bonds
  - In the resonance hybrid, the actual structure, all its C-C bonds equivalent, midway between double and single

Rules for Resonance Forms

- Individual resonance forms are imaginary - the real structure is a hybrid (only by knowing the contributors can you visualize the actual structure)
- Resonance forms differ only in the placement of their π or nonbonding electrons
- Different resonance forms of a substance don’t have to be equivalent
- Resonance forms must be valid Lewis structures: the octet rule applies
- The resonance hybrid is more stable than any individual resonance forms

Curved Arrows

- We can imagine that electrons move in pairs to convert from one resonance form to another
- A curved arrow shows that a pair of electrons moves from the atom or bond at the tail of the arrow to the atom or bond at the head of the arrow
Drawing Resonance Forms

- Start with one Lewis structure and push electrons to generate a new structure
- Pushable electrons are either non-bonding electrons or \( \pi \) electrons
- There must be a receptor site for the pushable electrons
- Receptors can be:
  - Atoms with a formal positive charge
  - Atoms that can tolerate a formal negative charge
  - Atoms which possess pushable electrons themselves

Examples

- The "enolate" derived from acetone

\[
\begin{align*}
\text{Acetone} & \quad \text{Acetone anion (enolate form)} \\
\text{This resonance form has the negative charge on oxygen.} & \quad \text{This resonance form has the negative charge on oxygen.}
\end{align*}
\]

- The anion derived from 2,4-pentanedione

\[
\begin{align*}
\text{2,4-Pentanedione} & \quad \text{2,4-Pentanedione anion (enolate form)} \\
\text{This resonance form has the negative charge on oxygen.} & \quad \text{This resonance form has the negative charge on oxygen.}
\end{align*}
\]

Acids and Bases

- Brensted-Lowery Theory
  - Acid is any species that donates \( H^+ \)
  - Base is any species that accepts \( H^+ \)

- Lewis Theory
  - Acids are electron acceptors or electrophiles
  - Bases are electron donors or nucleophiles
**Examples**

- **Brensted-Lowery**
  
  \[
  \text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{H}_2\text{O} + \text{NaCl}_{(aq)}
  \]
  
  \[
  \text{HCl}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4\text{Cl}_{(aq)}
  \]

- **Lewis**

  \[
  \text{BF}_3 + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{O}^+ + \text{BF}_3
  \]

**Brønsted Acids and Bases**

- "Brensted-Lowry" is usually shortened to "Brønsted"
- A **Brønsted acid** is a substance that donates a hydrogen ion \( \text{H}^+ \)
- A **Brønsted base** is a substance that accepts the \( \text{H}^+ \)
  “proton” is a synonym for \( \text{H}^+ \) - loss of an electron from H leaving the bare nucleus—a proton

**Quantitative Measures of Acid Strength**

- The equilibrium constant \( K_c \) for the reaction of an acid (HA) with water to form hydronium ion and the conjugate base (A⁻) is a measure related to the strength of the acid
- Stronger acids have larger \( K_c \)
- Note that brackets [ ] indicate concentration, moles per liter, M.

  \[
  \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+
  \]

  \[
  K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}
  \]
**$K_a$ – the Acidity Constant**

- The concentration of water as a solvent does not change significantly when it is protonated.
- The molecular weight of H$_2$O is 18 and one liter weighs 1000 grams, so the concentration is ~ 55.6 M at 25°C.
- The acidity constant, $K_a$ for HA, is 55.6 M (leaving $[\text{water}]$ out of the expression).
- $K_a$ ranges from $10^{15}$ for the strongest acids to very small values ($10^{-6}$) for the weakest.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = K_w[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

**$pK_a$ – the Acid Strength Scale**

- $K_a$ ranges from $10^{15}$ for the strongest acids to very small values ($10^{-6}$) for the weakest.
- $pK_a = \log K_a$.
- The larger the $pK_a$ value, the weaker the acid.
- A weak acid has a strong conjugate base.
- A weak base has a strong conjugate acid.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>$pK_a$</th>
<th>Strong/Weak</th>
<th>Strong/Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Water</td>
<td>15.72</td>
<td>Acidic</td>
<td>Basic</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
<td>3.38</td>
<td>Acid</td>
<td>Basic</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
<td>3.75</td>
<td>Acid</td>
<td>Basic</td>
</tr>
<tr>
<td>HF</td>
<td>Hydronitric acid</td>
<td>5.46</td>
<td>Acid</td>
<td>Basic</td>
</tr>
<tr>
<td>HCl</td>
<td>Nitric acid</td>
<td>1.38</td>
<td>Acid</td>
<td>Basic</td>
</tr>
</tbody>
</table>

**Table 2.2: Relative Strengths of Some Common Acids and Their Conjugate Bases**

- weaker acid
- stronger base
- weaker base
- stronger base
- stronger base
- stronger base
Organic Acids
- Those that lose a proton from O–H, such as methanol and acetic acid
- Those that lose a proton from C–H, usually from a carbon atom next to a C=O double bond (O=C–C–H)

Organic Bases
- Have an atom with a lone pair of electrons that can bond to H⁺
- Nitrogen-containing compounds derived from ammonia are the most common organic bases
- Oxygen-containing compounds can react as bases when with a strong acid or as acids with strong bases

Lewis Acid and Bases
- Reactions where no protons are involved can be thought of as acid/base reactions
- Reactions involve movement of electrons
- Lewis acids are electron pair acceptors and Lewis bases are electron pair donors
- The Lewis definition of acidity includes metal cations, such as Mg²⁺. They accept a pair of electrons when they form a bond to a base
- Group 3A elements, such as BF₃ and AlCl₃, are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases
- Transition-metal compounds, such as TiCl₃, FeCl₃, ZnCl₂, and SnCl₄, are Lewis acids
- Theory introduces concept of using arrows to push electrons
Lewis Acid-Base Reactions

Resonance and Acidity

- Phenols are weaker acids than carboxylic acids
- Why?
  - The anion is stabilized by four resonance structures
  - They are not all equivalent, unlike those for carboxylic acids
  - The three on the right are less important
  - Carbon is less electronegative than oxygen

Resonance and Basicity

- Aromatic amines usually less basic than aliphatic amines.
- Why?
  - Non-bonded pair is less available for sharing due to resonance
Drawing Chemical Structures

- Chemists use shorthand ways for writing structures
- Condensed structures: C-H and C-C and single bonds aren't shown but understood
  - If C has 3 H's bonded to it, write CH₃
  - If C has 2 H's bonded to it, write CH₂, and so on. The compound called 2-methylbutane, for example, is written as follows:
- Horizontal bonds between carbons aren't shown in condensed structures—the CH₃, CH₂, and CH units are shown simply but vertical bonds are added for clarity

Skeletal Structures

- Minimum amount of information but unambiguous
- C's not shown, assumed to be at each intersection of two lines (bonds) and at end of each line
- H's bonded to C's aren't shown — whatever number is needed will be there
- All atoms other than C and H are shown
Curved Arrow Formalism

- Curved arrow formalism is used to indicate the flow of electrons from the donor to the acceptor
- We used this method to keep track of electrons when drawing resonance structures
- We also used this to show flow of electrons in Lewis acid/base reactions
- We will describe organic reactions as Lewis acid/base reactions
- We will use the curved arrow formalism to write reaction mechanisms