Chapter 2

Polar Covalent Bonds; Acids and Bases

Bonding in Organic Compounds

• 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 bond occurs between atoms of identical electronegativity
• The greater the electronegativity difference, the greater the bond 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, $\delta^+$
  - Electronegative atom acquires partial negative charge, $\delta^-$

**Inductive effect:** shifting of electrons in a bond in response to EN of nearby atoms

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**Electrostatic Potential Map**

![Electrostatic Potential Map](image)

Chlorine: EN = 3.0
Carbon: EN = 2.5
Difference = 0.5

Electron poor  →  Electron rich
**Bond Dipole Moments**

- Bond polarity is measured by a quantity called dipole moment.
- \( \mu \) (dipole moment) = \( \delta \) (electric charge) \times d (distance)
- Expressed by a unit, **Debye (D)**
- Bond dipole moments can range from 0 to 3.6 D, the moment for C≡N
- A polar bond is thought of having a partial positive end (\( \delta^+ \)) and a partial negative end (\( \delta^- \))

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–O</td>
<td>0.86</td>
</tr>
<tr>
<td>C–F</td>
<td>1.51</td>
</tr>
<tr>
<td>C–Cl</td>
<td>1.56</td>
</tr>
<tr>
<td>C–Br</td>
<td>1.48</td>
</tr>
<tr>
<td>C–I</td>
<td>1.29</td>
</tr>
<tr>
<td>H–C</td>
<td>0.3</td>
</tr>
<tr>
<td>H–N</td>
<td>1.31</td>
</tr>
<tr>
<td>H–O</td>
<td>1.53</td>
</tr>
<tr>
<td>H–Cl</td>
<td>2.4</td>
</tr>
<tr>
<td>H–N</td>
<td>3.6</td>
</tr>
</tbody>
</table>

**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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O=O</td>
<td>( 180^\circ ) ( \mu = 0 ) D</td>
</tr>
<tr>
<td>H–O</td>
<td>( 104^\circ ) ( \mu = 1.84 ) D</td>
</tr>
<tr>
<td>CCl</td>
<td>all angles ( 109^\circ ) ( \mu = 0 ) D</td>
</tr>
<tr>
<td>ClH</td>
<td>all angles ( 109^\circ ) ( \mu = 1.86 ) D</td>
</tr>
</tbody>
</table>
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, $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{OCH}_3$ share the same molecular formula, $\text{C}_2\text{H}_6\text{O}$, but the atoms are bonded differently
- Geometric isomers have the same atom connectivity, but have different spatial placement of atoms
Problem

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

Problem: The compounds FCl and ICl have dipole moments that are similar in magnitude (0.9 and 0.7D, respectively) but opposite in direction. In one compound Cl is +ve end of the dipole; in the other it is the –ve end. Specify the direction of dipole moment in each compound and explain the reasoning behind your choice.

Order of Electronegativity in halogens is

\[ F > Cl > Br > I \]
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

Formal charge = \left( \frac{\text{Number of valence electrons in free atom}}{2} \right) - \left( \frac{\text{Number of bonding electrons}}{2} \right)

For the nitromethane nitrogen:

\[ \text{Formal charge} = \left( \frac{5}{2} \right) - \left( \frac{0}{2} \right) = \frac{5}{2} - 0 = +1 \]

For the singly bonded nitromethane oxygen:

\[ \text{Formal charge} = \frac{6}{2} - 6 = -1 \]

Problem

Calculate the formal charges of the atoms shown in red.

\[ \text{H}_2\text{C}^-\text{N}≡\text{N}: \]

\[ \text{H}_2\text{C}^+\text{N}≡\text{N}: \]
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 \( \pi \) 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 \((\text{C}_6\text{H}_6)\) 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 $\pi$ 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


- The anion derived from 2,4-pentanedione
Acids and Bases

• **Brønsted-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

• **Brønsted-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**
  \[
  \text{BF}_3 + \text{CH}_3\text{CH}_2\overset{-}{\text{O}}\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\overset{+}{\text{O}}\text{BF}_3
  \]
Brønsted Acids and Bases

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

Quantitative Measures of Acid Strength

- The equilibrium constant (Ke) 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 Ke
- 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 $H_2O$ is 18 and one liter weighs 1000 grams, so the concentration is $\sim 55.6$ M at 25°
- The acidity constant, $K_a$, for $HA$ is $55.6$ M (leaving [water] out of the expression)
- $K_a$ ranges from $10^{15}$ for the strongest acids to very small values ($10^{-60}$) for the weakest

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

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

**p$K_a$ – the Acid Strength Scale**

- $K_a$ ranges from $10^{15}$ for the strongest acids to very small values ($10^{-60}$) 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>Name</th>
<th>$pK_a$</th>
<th>Conjugate base</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weaker acid</td>
<td>$H_2O$</td>
<td>15.71</td>
<td>$H_3O^+$</td>
<td>Hydronium ion</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>4.31</td>
<td>$CN^-$</td>
<td>Cyanide ion</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid</td>
<td>4.76</td>
<td>$Cl_2CO_2^-$</td>
<td>Acetate ion</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>3.45</td>
<td>$F^-$</td>
<td>Fluoride ion</td>
</tr>
<tr>
<td></td>
<td>Nitric acid</td>
<td>1.3</td>
<td>$NO_3^-$</td>
<td>Nitrate ion</td>
</tr>
<tr>
<td>Stronger acid</td>
<td>$HCl$</td>
<td>7.0</td>
<td>$Cl^-$</td>
<td>Chloride ion</td>
</tr>
</tbody>
</table>

*Table 2.3: Relative Strengths of Some Common Acids and Their Conjugate Bases*
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 TiCl₄, 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

![Chemical structures showing resonance](image)

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

![Condensed structure of 2-methylbutane](image)
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 are not shown – whatever number is needed will be there
- All atoms other than C and H are shown
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 use the curved arrow formalism to write reaction mechanisms.