Milestones of organic chemistry: structural theory (notes of Sept. 9) and electronic theory of organic chemistry

Inability of the structural theory of organic chemistry to rationalize the chemical reactivity of carbon compounds

**Electronic theory of organic chemistry**: an intellectual framework that allows one to rationalize and predict the chemical reactivity of organic compounds on the basis of the electronic properties of their molecules (= how electrons behave within a molecule)

Principle: the electronic theory permits an approach to mastering organic chemistry that relies on logical reasoning, not on memorization.

Fundamental principles of the electronic theory of organic chemistry:

(i) A "reaction" is a movement of electrons.

(ii) During a reaction, electrons move under the influence of electrostatic fields; i.e., from regions of negative charge to regions of positive charge.

(iii) More accurately, electrons always move from an orbital of high electronic density (the "donor orbital": a fully or partially occupied orbital) to one of low electronic density (the "acceptor orbital": an unoccupied or partially occupied orbital).

(iv) Electron movement from one orbital to another is allowed only for certain relative orientations of donor and acceptor orbitals.

Electrostatic properties of molecules as important factors that influence their reactivity

Evaluating the electrostatic properties of molecules: formal charges, bond polarization, and oxidation states

Principle: atoms can produce bonded states in which significant electrostatic imbalance exists

Formal charge of an atom in a molecule: a parameter that indicates whether that atom is electrostatically balanced or imbalanced

The formal charge on an atom is calculated by:

(i) assuming that all the bonds in which the atom participates are covalent;

(ii) counting the total number of valence electrons that the atom contributes to the various bonds in which it participates; and

(iii) deciding whether these valence electrons balance out the nuclear charge, or are in deficit, or in surplus.
The case of CH₄, NH₄, and BH₄

**The formal charge on the C atom in methane, CH₄**

**Step 1**: draw a complete Lewis structure of the molecule (electron dots, ...):

```
   H
  H   C   H
  H
```

**Step 2**: count the number of valence electrons around the atom of interest.

Each atom in a bonded pair of atoms has contributed one of its valence electrons to the electron pair that we call "bond." If we "shatter" the molecule so that each atom in a bonded pair retrieves one of the two electrons that form the bond (i.e., if we "undo" covalent bonds) we will see how many valence electrons were present around each atom prior to bond formation:

```
  H
  H   C   H   "shatter"
  H
```

Conclusion: the C atom in methane is surrounded by 4 valence electrons

**Step 3**: determine whether valence electrons cancel the nuclear charge out.

* Carbon is in group 4 of the periodic table, so it requires 4 valence electrons to balance out the nuclear charge.
* The C atom in methane has 4 valence electrons
* The C atom in methane is electrostatically balanced

**Conclusion**: the formal charge on C in methane is zero

Notice that the formal charge on each H atom is also zero. Indeed, H atoms in any covalent molecule have always zero formal charge, as readily determined though the above logic.

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**The formal charge on the N atom in NH₄**

**Step 1**: draw a complete Lewis structure of the molecule:

```
   H
  H   N   H
  H
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**Step 2**: count the number of valence electrons around the atom of interest.
Step 3: determine whether valence electrons balance out the nuclear charge.

• N is in group 5: it needs 5 valence electrons to balance out the nuclear charge.
• The N atom in NH₄ has 4 valence electrons: 1 fewer than it should.
• The N atom in NH₄ is electrostatically imbalanced.

Important: formal charges are integral parts of a chemical structure and must be clearly indicated. This is done with encircled + or – signs. So, the correct way to draw NH₄ is:

Why "formal" charge? Rigorously speaking, the + 1 charge present in NH₄⁺ is delocalized all over the molecule, i.e., each atom (N and 4 H’s in this case) bears a share of it. But for simplicity, it is convenient to think of it as if it were localized on the N atom. That’s why one calls it a formal charge: because for chemical reasoning it is best to think of it as formally residing on the N atom.

The formal charge on the B atom in BH₄

Step 1: draw a complete Lewis structure of the molecule:

\[ \text{BH}_4 = \begin{array}{c} \text{H} \\ . \\ \text{H} \cdot \text{B} \cdot \text{H} \\ \cdot \\ \text{H} \end{array} \]

Step 2: count the number of valence electrons around the atom of interest.

\[ \text{H} \\ . \\ \begin{array}{c} \text{H} \cdot \text{B} \cdot \text{H} \\ . \\ \text{H} \end{array} \]

Step 3: determine whether valence electrons balance out the nuclear charge.

• B is in group 3: it needs 3 valence electrons to balance out the nuclear charge.
• The B atom in BH₄ has 4 valence electrons: 1 more than it should.
• The B atom in BH₄ is electrostatically imbalanced.
Electronegativity and bond polarization

Permanent dipole moments (=electrostatic fields) within molecules displaying bonded atoms of unequal electronegativity

Reminder: the electronegativity of first-row elements starts at 1.0 with Li and it increases by 0.5 units per column:

\[
\begin{align*}
\text{Li} &= 1.0; \\
\text{Be} &= 1.5; \\
\text{B} &= 2.0; \\
\text{C} &= 2.5; \\
\text{N} &= 3.0; \\
\text{O} &= 3.5; \\
\text{F} &= 4
\end{align*}
\]

Influence of permanent dipole moments on the chemical reactivity of a molecule; in particular, on the ability of that molecule to accept or donate electrons during chemical reactions.

Example: consider a C–Cl bond. The e.n. of C is \( \approx 2.5 \); that of Cl \( \approx 3.2 \) Therefore, the C–Cl bond will be polarized toward Cl; i.e., the Cl atom is the negative end of the dipole, while the C atom is the positive end thereof:

\[\delta^+ \text{C} \quad \delta^- \text{Cl}\]

electron cloud in the bond is distorted toward the Cl atom

imagine an electron-rich, electrostatically negative agent approaching the above C–Cl bond in the course of a chemical reaction: will it interact preferentially with the C or the Cl atom? Obviously, the incoming agent will be electrostatically attracted to the C atom, but repelled by the Cl atom. We may anticipate that the C atom is likely to behave as an electron acceptor. By the same logic, the Cl atom is likely to behave as an electron donor.

Principle: as a result of bond polarization, an atom in a molecule may acquire more electronic density than necessary to balance out its nuclear charge (see the Cl atom above), i.e., it may acquire a partial negative charge. Likewise, always as a result of bond polarization, an atom in a molecule may be left with insufficient electron density to balance out its nuclear charge (see the C atom above), i.e., it may acquire a partial positive charge.

Oxidation state: a parameter that describes to what extent an atom in a bonded state has acquired/lost electronic density.

The oxidation state of an atom in a generic molecule as the algebraic sum of bond polarization and formal charge

Example: the oxidation state of C in \( \text{CH}_4 \), \( \text{CF}_4 \), and \( \text{CH}_3\text{F} \)
• the formal charge on C is zero
• C is more electronegative than H (2.5 vs. 2.1)
• Formally, C has "stolen" 1 electron from each of the 4 H's
• Formally, C has acquired 4 extra electrons in this bonded state

Sum of bond polarization and formal charges for C:
4 x (-1) [bond polarization] + 0 [formal charge on C]

The oxidation state of C in CH₄ is −4

• the formal charge on C is zero
• C is more electronegative than H (2.5 vs. 2.1) and less electronegative than F (2.5 vs. 4)
• Formally, C has "stolen" 1 electron from each of the 3 H's and "lost" 1 electron to the F atom
• Overall, C has formally gained 2 extra electrons in this bonded state

Sum of bond polarization and formal charges for C:
3 x (-1) + (1) [bond polarization] + 0 [formal charge on C]

The oxidation state of C in CH₃F is −2

• the formal charge on C is zero
• C is less electronegative than F (2.5 vs. 4)
• Formally, C has "lost" 1 electron to each of the F atoms
• Overall, C has formally lost 4 electrons in this bonded state

Sum of bond polarization and formal charges for C:
4 x (+1) [bond polarization] + 0 [formal charge on C]

The oxidation state of C in CF₄ is +4

Note: in the above molecules, the oxidation state of H is +1, and that of F is −1