1.5: Formal Charge

Learning Objectives

- Calculate the formal charge on atoms in organic molecules.
- Understand the geometry of and the location of valence electrons in the hybrid orbitals of species with formal positive charge, formal negative charge, and organic radicals.

Prelude to a formal charge

Isolated atoms are neutral because they have equal protons and electrons. When an atom loses a a valence electron it becomes +ve species or cation, e.g., Na after loosing an electron becomes Na^{+}, and Ca after loosing two electron becomes Ca^{2+}. When an atom gains a valence electron, it becomes -ve species or anion, e.g., Cl after gaining an electron becomes Cl^{-}, and O after gaining two electrons becomes O^{2-}. Covalently bonded species can also be ions, e.g., NH_3^{+}, and $\mathrm{H_3O}^{+}$ are cations, and HO^{-}, and CO_2^{2-} are anions. Organic compounds often become ions as intermediates in reactions.

What is the formal charge?

A formal charge is assigned to an atom in a molecule based on the assumption that bonding electrons are shared equally.

How to calculate the formal charge?

The formal charge is calculated by subtracting an atom's valence electrons in a molecule from the valence electron of the isolated atom. Valence electrons of an isolated atom are equal to the first digit of the group number in the periodic table. For example, H is in group 1 and has one valence electron shown as: $\dot{\mathrm{H}}$ in Lewis symbol. C is in group 14 and has four valence electrons shown as: $\cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot$, i.e., four unpaired dots in its Lewis symbol. N is in group 15 and has five valence electrons shown as: $\cdot\ddot{\underset{\cdot}{\mathrm{N}}}\cdot$, i.e., five dots (one paired and three unpaired) in its Lewis symbol. Halogens are in group 17 and have seven valence electrons, e.g. $\cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$, i.e., shown as three paired and one unpaired dots. Valence electrons in a molecule are assigned to an atom, assuming that the bonding electrons are equally shared, i.e., one electron to the atom per one bond. All the nonbonding electrons are assigned to the atom they are on.

The formula for calculating formal charge is:

$$Fc = Ve - (B + Nb)$$

, where Fc is the formal charge, Ve is the valence electrons in an isolated atom, B is the number of bonds attached to the atom, and Nb is nonbonding electrons on the atom in the molecule.

Example 1.5.1

What is the formal charge on C in methane ($\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}$).

Solution

Isolated C has four valance electrons, there are four bonds and no nonbonding electron in the molecule, so: Ve = 4, B = 4, Nb = 0

$Fc = Ve - (B + Nb)$ = 4 - (4 + 0) = 0

Answer: 0 formal charge, i.e., C in methane ($\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}^{0}}}-\mathrm{H}$), where superscript over the atom (C in this case) show the formal charge

Reactive intermediates and their formal charges

If one of the $\mathrm{C-H}$ bonds in an organic compound breaks, three situations may arise, e.g., for $\mathrm{H-\underset{H}{\overset{H}{C}}-H}$ the situations are:

1. one of the bonding electrons may remain on the C, i.e., $(\mathrm{H-\underset{H}{\dot{C}}-H})$,
2. none of the bonding electrons may remain on the C, i.e, $(\mathrm{H-\underset{H}{C}-H})$, and
3. both the bonding electrons may remain on the C, i.e., $(\mathrm{H-\underset{H}{\ddot{C}}-H})$.

Each of these situations results in a C with three bonds which are reactive intermediates. They are short-lived and tend to react to re-establish regular four bonds around the C. Figure $1.5.1$ shows the structure and hybridization of the reactive carbon species. A specie with a single unshared electron on an atom is a free radical that tends to make a covalent bond by sharing the electron. A $\mathrm{H-\underset{H}{\dot{C}}-H}$ is an example of a free. The $(\mathrm{H-\underset{H}{\dot{C}}-H})$, is sp^2 hybridized with three bonds and an unshared electron in its p-orbital, as illustrated in Figure $1.5.1$a.

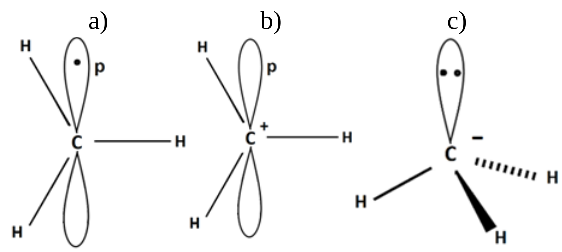

Figure $1.5.1$: Illustration of a) a free radical $\mathrm{H-\underset{H}{\dot{C}}-H}$ that is sp^2 hybridized with three $\sigma_{sp^2\text{-}s}$ bonds, and a p-orbital occupied by a single electron, b) a carbocation $\mathrm{H-\underset{H}{\overset{+}{C}}-H}$ that is sp^2 hybridized with three $\sigma_{sp3\text{-}s}$ bonds, and a vacant p-orbital, and c) a cabanion $\mathrm{H-\underset{H}{\overset{-}{\ddot{C}}}-H}$ this is sp^3 hybridized with three $\sigma_{sp^3\text{-}s}$ bond and one sp^3 orbital occupied by a lone pair. (Copyright; Public domain)

Example $1.5.2$

What is the formal charge on C in $\mathrm{H-\underset{H}{\dot{C}}-H}$.

Solution

Isolated C has four valance electrons, there are three bonds and one nonbonding electron on C in the molecule, so: Ve = 4, B = 3, Nb = 1

$Fc = Ve - (B + Nb)$ = 4 - (3 + 1) = 0

Answer: 0 formal charge, i.e. C in $\mathrm{H-\underset{H}{\dot{C}^{0}}-H}$.

Example $1.5.3$

What is the formal charge on C in $\mathrm{H-\underset{H}{C}-H}$.

Solution

Isolated C has four valance electrons, there are three bonds and no nonbonding electron on C in the molecule, so: Ve = 4, B = 3, Nb = 0

$Fc = Ve - (B + Nb)$ = 4 - (3 + 1) = +1

Answer: +1 formal charge, i.e. ($\mathrm{H{-}\overset{+1}{\underset{|\atop H}{C}}{-}H}$).

Example 1.5.4

What is the formal charge on C in $\mathrm{H{-}\underset{|\atop H}{\ddot{C}}{-}H}$.

Solution

Isolated C has four valance electrons, and there are three bonds and two nonbonding electrons on C in the molecule, so: V_e = 4, B = 3, N_b = 2

$Fc = Ve - (B + Nb)$ = 4 - (3 + 2) = -1

Answer: 0 formal charge, i.e. $\mathrm{H{-}\underset{|\atop H}{\ddot{C}}^{-1}{-}H}$.

- A radical is a C with three bonds and one unshared electron. C in $\mathrm{H{-}\underset{|\atop H}{\dot{C}}{-}H}$ is an example of a radical that is sp^2 hybridized with three bonds and a p-orbital is partially filled by a single electron, as illustrated in Figure 1.5.1a. A radical tends to make a bond by accepting an electron in its partially filled p-orbital.
- A carbocation is a C with three bonds and no unshared electrons. A $\mathrm{H{-}\overset{+1}{\underset{|\atop H}{C}}{-}H}$ is an example of carbonation that is sp^2 hybridized with three bonds and a vacant p-orbital, as illustrated in Figure 1.5.1b. A carbocation tends to make a bond by accepting a lone pair in its vacant p-orbital.
- A carbanion is a C with three bonds and two unshared electrons. $\mathrm{H{-}\underset{|\atop H}{\ddot{C}}^{-1}{-}H}$ is an example of a carbanion that is sp^3 hybridized with three bonds and the fourth sp^3 orbital occupied by a lone pair, as illustrated in Figure 1.5.1c. A carbanion tends to make a bond by donating the lone pair.

Species containing N and O with formal charges

N has three bonds and one lone pair, e.g., in ammonia $\mathrm{H{-}\underset{|\atop H}{\ddot{N}}{-}H}$ and O has two bonds and two lone pairs, e.g., water $\mathrm{H{-}\underset{|\atop H}{\ddot{O}}{:}}$ molecule. One more bond results in a cation, and one fewer bond results in anion species, as shown by solving the formal charges in the following examples.

Example 1.5.5

What is the formal charge on a) N in $\mathrm{H{-}\underset{|\atop H}{\ddot{N}}{-}H}$ and b) on O in $\mathrm{H{-}\underset{|\atop H}{\ddot{O}}{:}}$

Solution

a) Isolated N has five valance electrons, there are three bonds and two nonbonding electrons (a lone pair) in the molecule, so: Ve = 5, B = 3, Nb = 2

$Fc = Ve - (B + Nb)$ = 5 - (3 + 2) = 0

Answer: 0 formal charge, i.e., N in $\mathrm{H{-}\underset{|\atop H}{\ddot{N}}^{0}{-}H}$

a) Isolated O has six valance electrons, there are two bonds and four nonbonding electrons (two lone pairs) in the molecule, so: Ve = 6, B = 2, Nb = 4

$Fc = Ve - (B + Nb)$ = 6 - (2 + 4) = 0

Answer: 0 formal charge, i.e., N in O in $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\bullet\bullet}{O}}{:}^{0}}$

✔ Example 1.5.6

What is the formal charge on a) N in $(\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}{-}H})$ and b) on O in $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\bullet\bullet}{O}}{-}H}$

Solution

a) Isolated N has five valance electrons, there are four bonds and no nonbonding electrons in the molecule, so: Ve = 5, B = 4, Nb = 0

$Fc = Ve - (B + Nb)$ = 5 - (4 + 0) = +1

Answer: +1 formal charge, i.e., N in N in $(\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}^{+1}{-}H})$

a) Isolated O has six valance electrons, there are three bonds and two nonbonding electrons (one lone pair) in the molecule, so: Ve = 6, B = 3, Nb = 2

$Fc = Ve - (B + Nb)$ = 6 - (3 + 2) = +1

Answer: +1 formal charge, i.e., O in $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\bullet\bullet}{O}}^{+1}{-}H}$

✔ Example 1.5.7

What is the formal charge on a) N in $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\bullet\bullet}{N}}{:}}$ and b) on O in $\mathrm{H{-}\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}{:}}$

Solution

a) Isolated N has five valance electrons, there are two bonds and four nonbonding electrons (two lone pairs) in the molecule, so: Ve = 5, B = 2, Nb = 4

$Fc = Ve - (B + Nb)$ = 5 - (2 + 4) = -1

Answer: -1 formal charge, i.e. N in $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\bullet\bullet}{N}}{:}^{-1}}$

a) Isolated O has six valance electrons, there is one bond and six nonbonding electrons (three lone pair) in the molecule, so: Ve = 6, B = 1, Nb = 6

$Fc = Ve - (B + Nb)$ = 6 - (1 + 6) = -1

Answer: +1 formal charge, i.e., O in $\mathrm{H{-}\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}{:}^{-1}}$

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