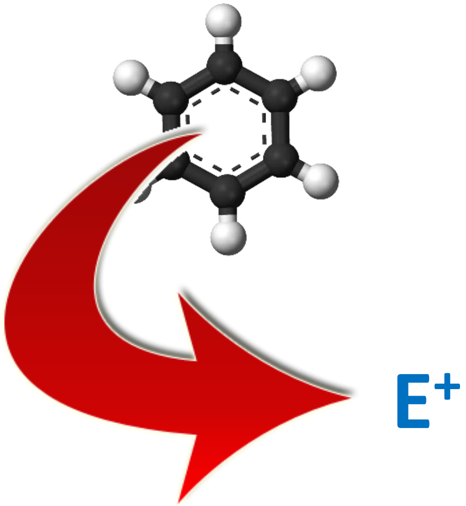
LECTURE

4

Introduction to Organic Reactions and Their Mechanisms



Department of General Science, Faculty of Education,
Suan Sunandha Rajabhat University

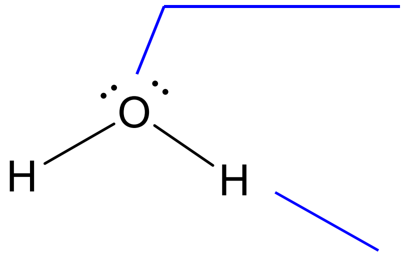
Outline

- ☐ Formal charge
- ☐ Resonance Theory
- ☐ Predicting the Strength of Acids and Bases
- ☐ Acids and Bases
- ☐ Lewis acid and Lewis bases
- ☐ Nucleophiles Vs Electrophiles
- ☐ How to Use Curved Arrows in Illustrating Reactions

Formal Charges

How to calculate formal charges

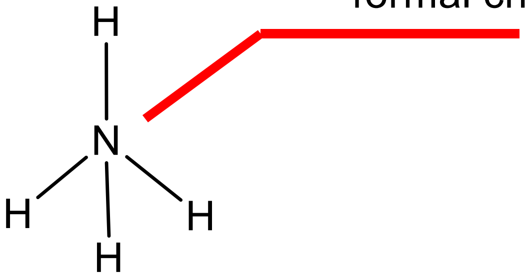
Formal charge = The number of Valence electron - the number of electrons surrounding an atom



formal charge = 6 - 6 =0

formal charge = 1 - 1 =0

Formal charge part 1

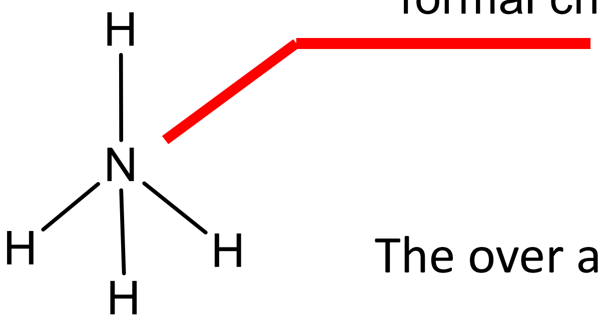


formal charge = 5 - 4 = +1

Formal charge part 2

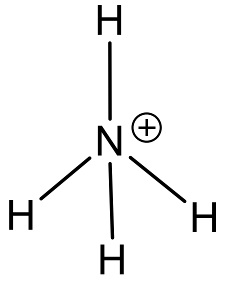
Formal Charges

Ammonium ion (NH_4^+)

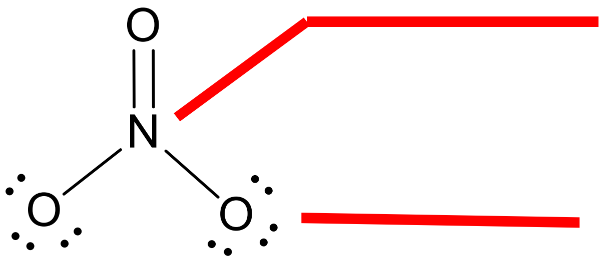


formal charge = 5 - 4 = +1

The over all charge on ion is +1



Nitrate ion (NO_3^-)

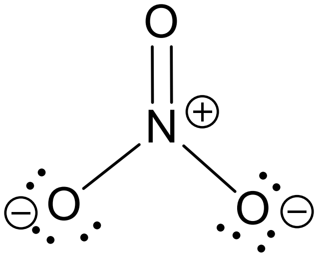


formal charge = 5 - 4 = +1

formal charge = 6 - 7 = -1

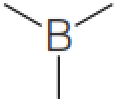
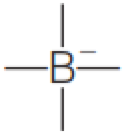
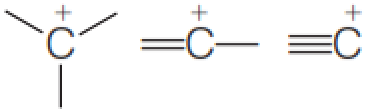
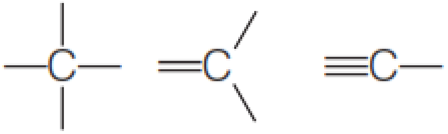
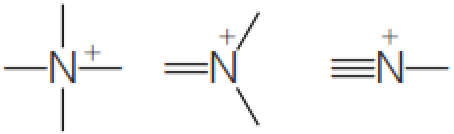
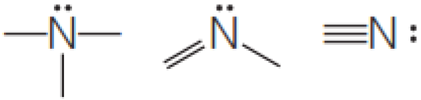
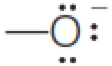
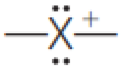
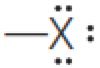
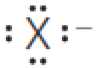
formal charge = 6 - 7 = -1

over all charge = -1



Formal Charges

TABLE 1.3 A Summary of Formal Charges

Group	Formal Charge of +1	Formal Charge of 0	Formal Charge of −1
IIIA			
IVA			
VA			
VIA			
VIIA		 (X = F, Cl, Br, or I)	

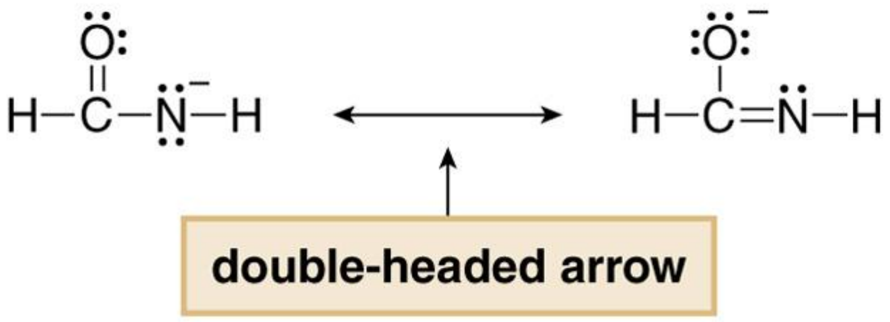
Reference: Solomons, T. W. G.; Fryhle, C. *Organic Chemistry; John Wiley & Sons, 2009.*

Resonance

Resonance

***Resonance structures*/ Resonance forms** are two Lewis structures having the same placement of atoms but a different arrangement of electrons.

- Some molecules cannot be adequately represented by a single Lewis structure. For example:

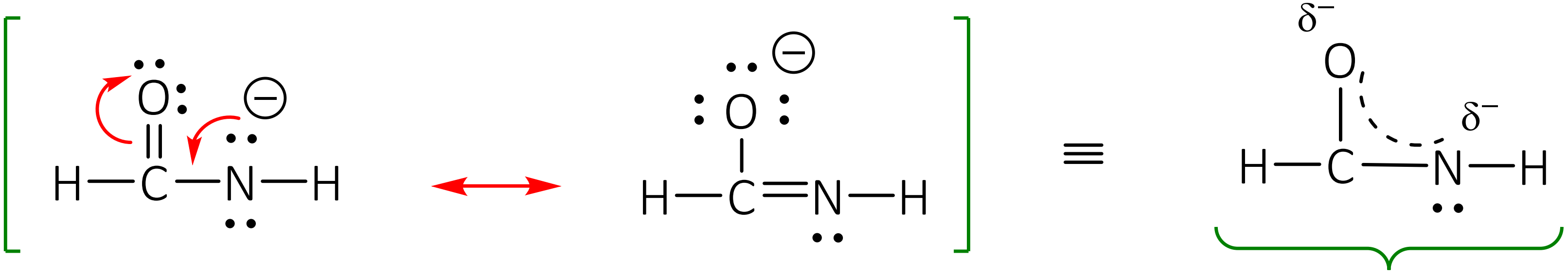


A double-headed arrow is used to separate the two resonance structures

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Which resonance structure is an accurate representation for [HCONH⁻] ?

- The answer is *Neither of them*



Combined representation (resonance hybrid)

The hybrid shows characteristics of both structures

- Resonance allows certain electron pairs to be delocalized over two or more atoms, and this delocalization adds stability.
- A molecule with two or more resonance forms is said to be **resonance stabilized**.

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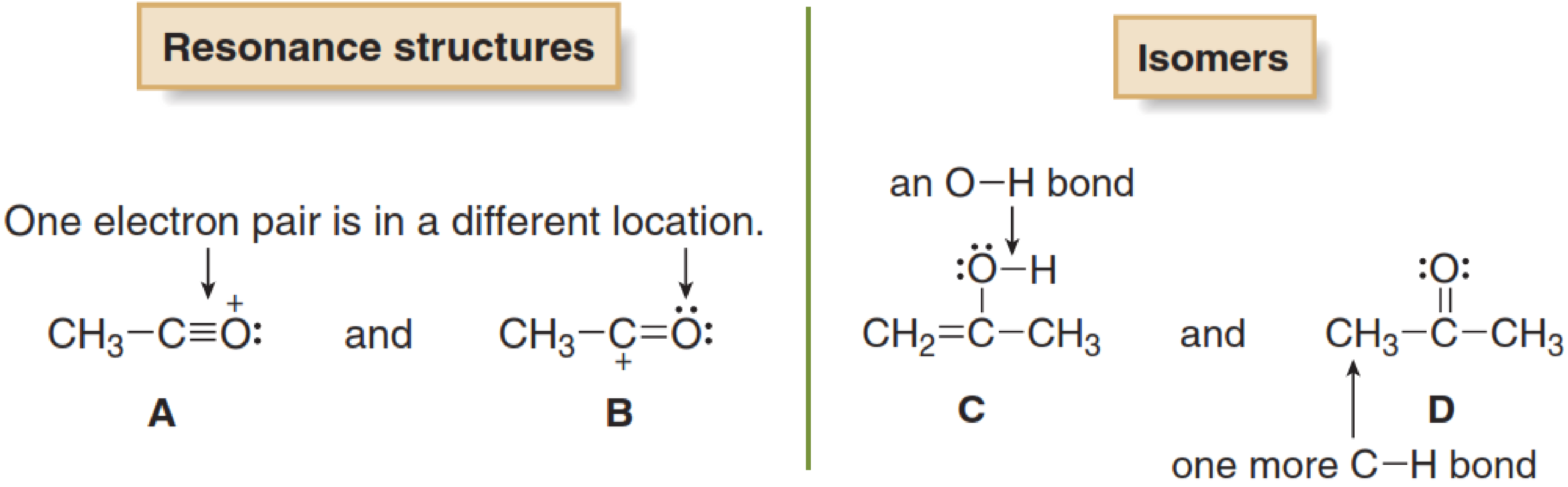
Basic Principles of Resonance Theory

- ***Resonance structures are not real***. An individual resonance structure does not accurately represent the structure of a molecule or ion. *Only the hybrid does!*.
- **Resonance structures are not in equilibrium with each other**. There is no movement of electrons from one form to another.
- ***Resonance structures are not isomers.***



$CH_3-C\equiv\overset{+}{\ddot{O}}:$ and $CH_3-\underset{+}{C}=\ddot{O}:$

$CH_2=\overset{:\ddot{O}-H}{\overset{|}{C}}-CH_3$ and $CH_3-\overset{:O:}{\overset{\|}{C}}-CH_3$

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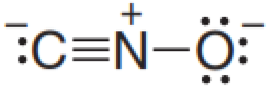
Sample Problem 1.1

Question: Classify each pair of compound as isomer or resonance structure.

a.

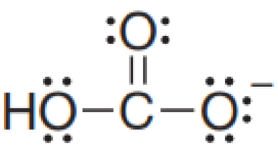
$^{-}:\ddot{N}=C=\ddot{O}:$

and



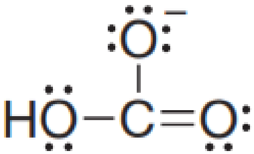
$^{-}:C\equiv\overset{+}{N}-\ddot{\underset{..}{O}}:^{-}$

b.



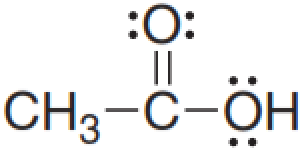
$H\ddot{\underset{..}{O}}-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}:^{-}$

and



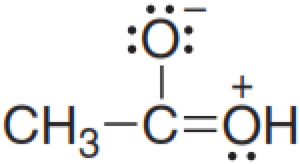
$H\ddot{\underset{..}{O}}-\overset{\overset{:\ddot{O}:^{-}}{|}}{C}=\underset{..}{O}:$

C.



$CH_3-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{O}}H$

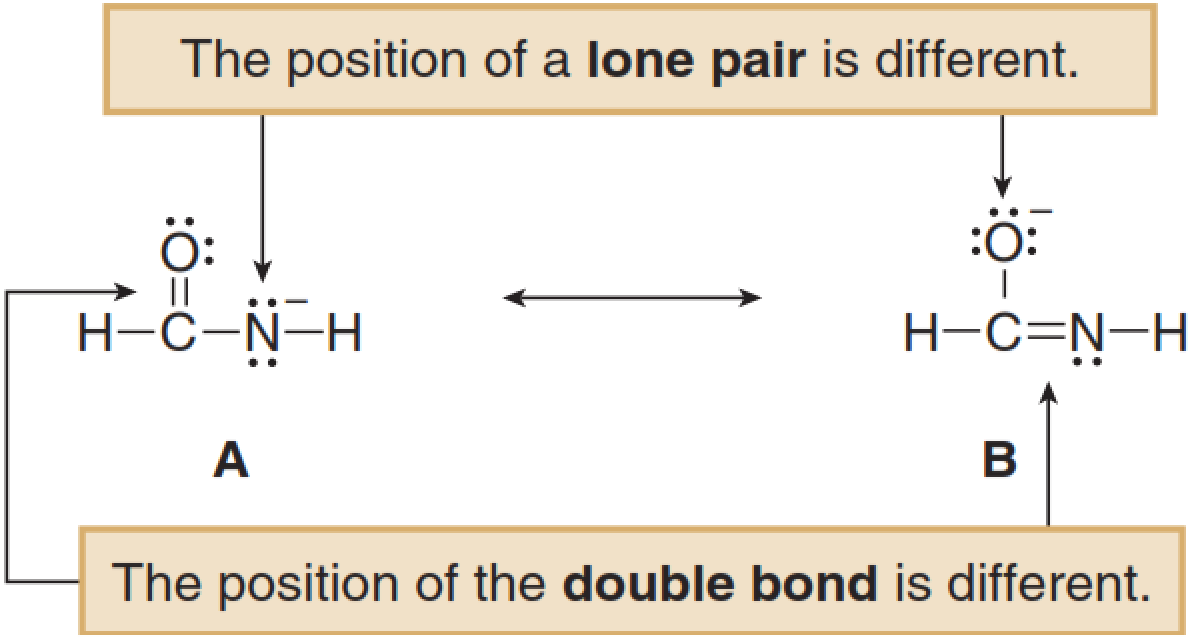
and



$CH_3-\overset{\overset{:\ddot{O}:^{-}}{|}}{C}=\overset{+}{\underset{..}{O}}H$

Drawing Resonance Structures

Rule [1]: Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.



The position of a **lone pair** is different.

$\mathrm{H{-}\overset{\overset{\ddot{O}:}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{N}}^{-}{-}H} \longleftrightarrow \mathrm{H{-}\overset{\overset{:\ddot{O}:^{-}}{|}}{C}{=}\underset{\cdot\cdot}{N}{-}H}$

A **B**

The position of the **double bond** is different.

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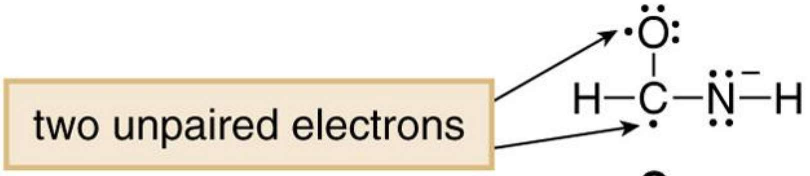
Drawing Resonance Structures

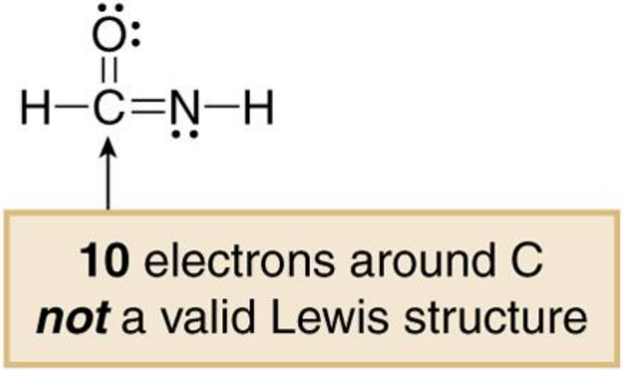
Rule [2]: Two resonance structures must have the same number of unpaired electrons.



C

- **A** and **B** have no unpaired electrons.
- **C** is ***not*** a resonance structure of **A** and **B.**

Rule [3]: Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight electrons.



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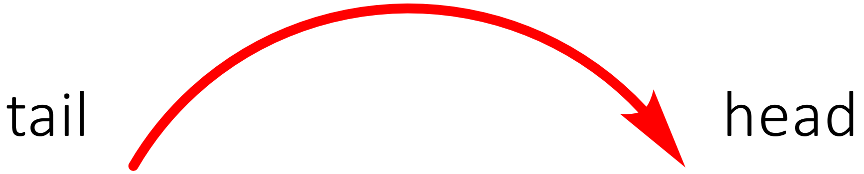
Curved Arrow Notation

- Curved arrow notation is a convention that shows how electron position differs between two resonance forms.

- Curved arrow notation shows the movement of an electron pair.



always begins at the ***electron pair***, either in a **bond** or **lone pair**.

The head points to where the electron pair “moves.”

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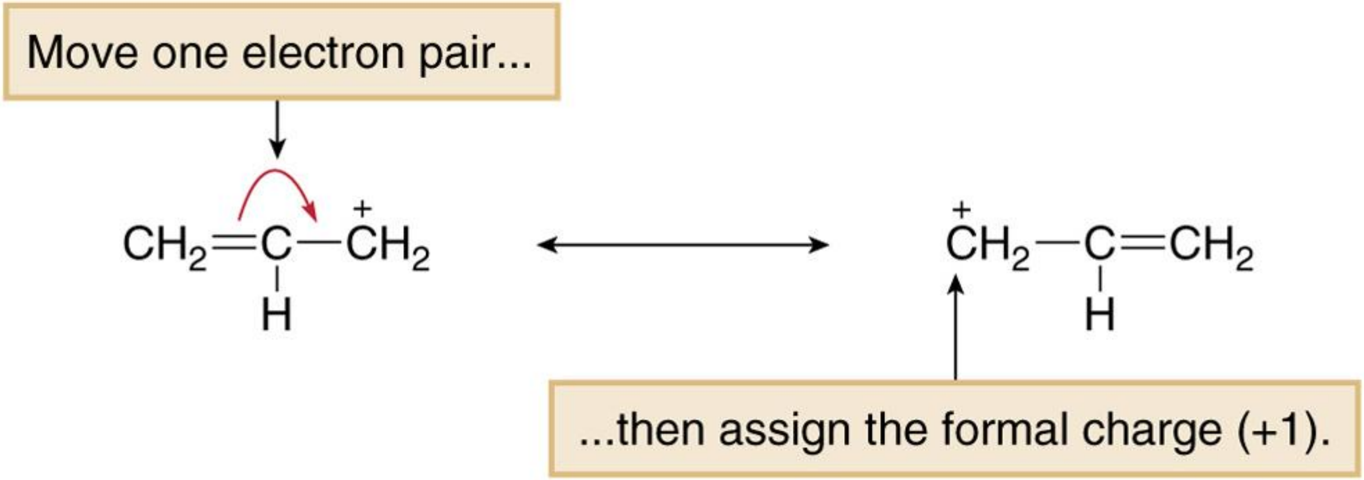
Curved Arrow Notation

Example 1

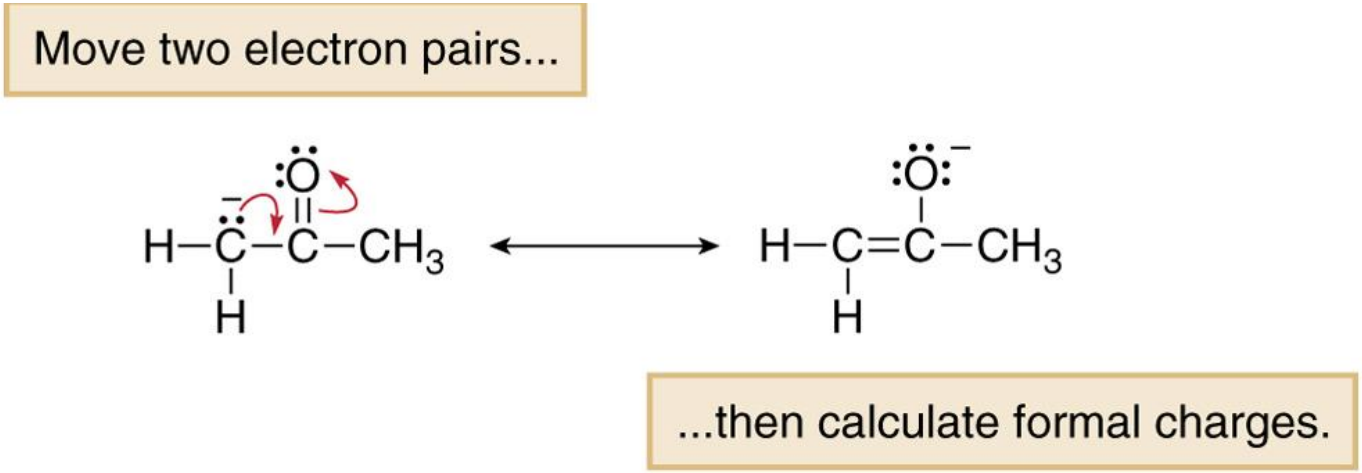


Move one electron pair...

$$\mathrm{CH_2{=}\underset{\underset{\displaystyle H}{|}}{C}{-}\overset{+}{C}H_2} \longleftrightarrow \mathrm{\overset{+}{C}H_2{-}\underset{\underset{\displaystyle H}{|}}{C}{=}CH_2}$$

...then assign the formal charge (+1).

Example 2



Move two electron pairs...

$$\mathrm{H{-}\underset{\underset{\displaystyle H}{|}}{\overset{-}{\ddot{C}}}{-}\overset{\overset{\displaystyle :\ddot{O}}{\|}}{C}{-}CH_3} \longleftrightarrow \mathrm{H{-}\underset{\underset{\displaystyle H}{|}}{C}{=}\overset{\overset{\displaystyle :\ddot{O}:^{-}}{|}}{C}{-}CH_3}$$

...then calculate formal charges.

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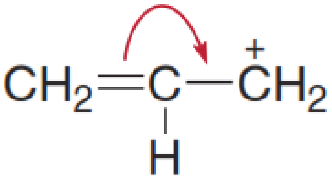
Sample Problem 1.13

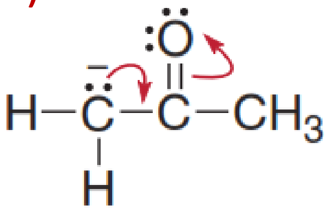
Question: Follow the curved arrows to draw a second resonance structure for each ion

(a)



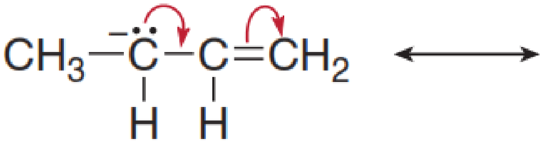
$CH_2{=}\underset{H}{C}{-}\overset{+}{C}H_2$

(b)



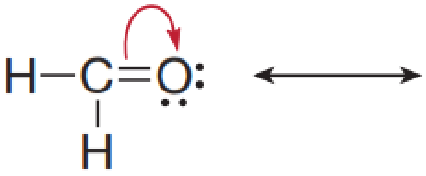
$H{-}\underset{H}{\overset{-\,\ddot{}}{C}}{-}\overset{\ddot{O}:}{\overset{\|}{C}}{-}CH_3$

(c)



$CH_3{-}\underset{H}{\overset{-\,\ddot{}}{C}}{-}\underset{H}{C}{=}CH_2 \longleftrightarrow$

(d)



$H{-}\underset{H}{C}{=}\ddot{O}: \longleftrightarrow$

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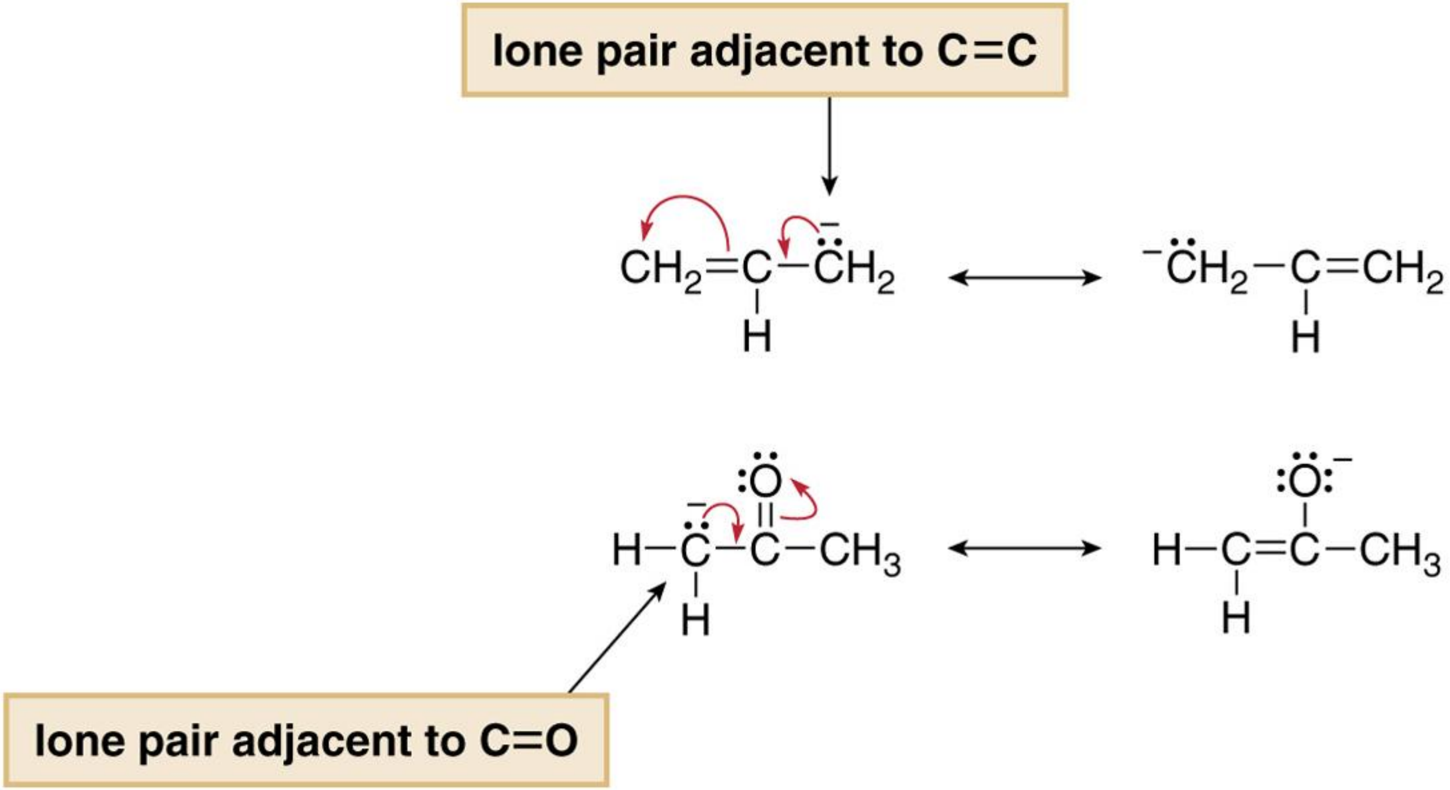
Occurrence of Resonance

- Two different resonance structures can be drawn when a lone pair is located on an atom directly bonded to a double bond.



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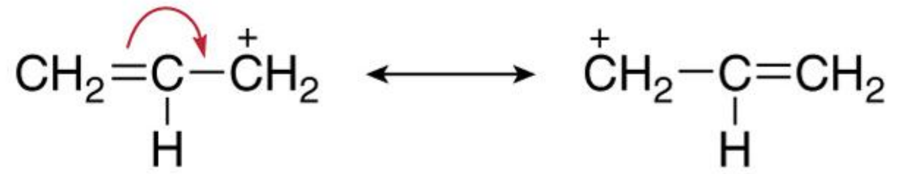
Occurrence of Resonance

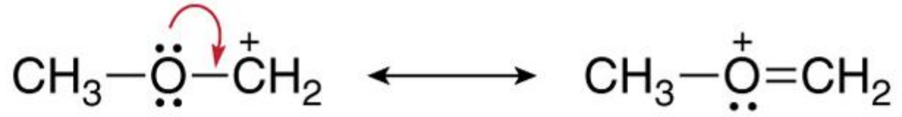
❑ Multiple resonance structures can also be drawn when an atom bearing a (+) charge is bonded either to a double bond or an atom with a lone pair.

(+) charge adjacent to a double bond



$$CH_2=\underset{H}{\underset{|}{C}}-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-\underset{H}{\underset{|}{C}}=CH_2$$

(+) charge adjacent to an atom with a lone pair



$$CH_3-\underset{..}{\ddot{O}}-\overset{+}{C}H_2 \longleftrightarrow CH_3-\underset{..}{\overset{+}{O}}=CH_2$$

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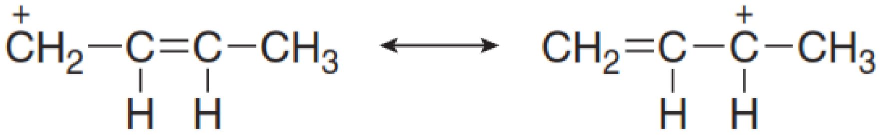
Sample Problem 1.14

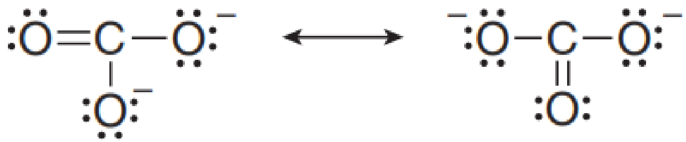
Question: Use curved arrow notation to show how the first resonance structure can be converted to the second

(a)

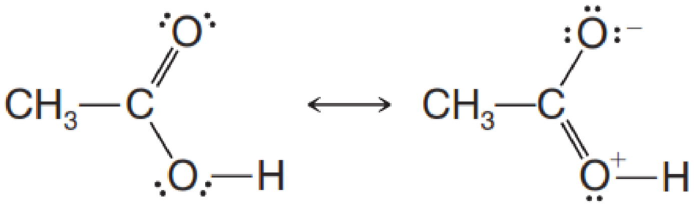


$\overset{+}{C}H_2-\underset{H}{C}=\underset{H}{C}-CH_3 \longleftrightarrow CH_2=\underset{H}{C}-\underset{H}{\overset{+}{C}}-CH_3$

(b)



(d)



(c) $\overset{+}{C}H_2-\ddot{N}(CH_3)_2 \longleftrightarrow CH_2=\overset{+}{N}(CH_3)_2$

(e) $:NH_2-C\equiv N: \longleftrightarrow \overset{+}{N}H_2=C=\ddot{N}:^{-}$

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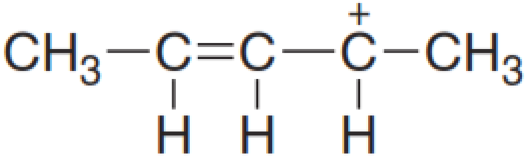
Sample Problem 1.15

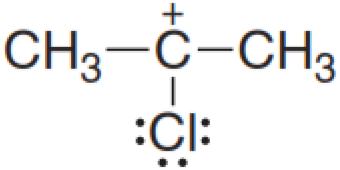
Question: Draw a second resonance structure for each species

a.



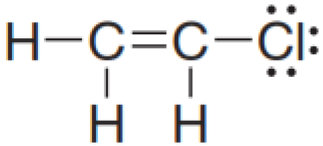
$CH_3-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{+}{C}}-CH_3$

b.



$CH_3-\underset{:\underset{..}{Cl}:}{\overset{+}{C}}-CH_3$

c.



$H-\underset{H}{C}=\underset{H}{C}-\underset{..}{\ddot{Cl}}:$

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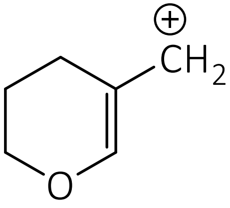
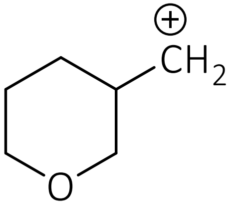
Sample Problem 1.16

Question: Determine which ion is more stable

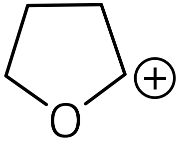
Example:



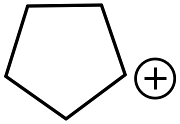
Vs



(a)

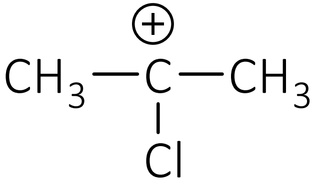


Vs



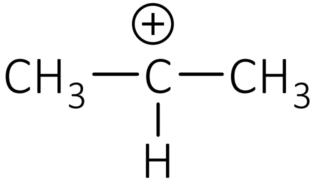
(b) $^{\ominus}\ddot{C}H_2-\underset{\cdot\cdot}{\ddot{O}}-CH_3$ Vs $^{\ominus}\ddot{C}H_2-C\equiv N:$

(c)



$CH_3-\overset{\oplus}{\underset{Cl}{C}}-CH_3$

Vs

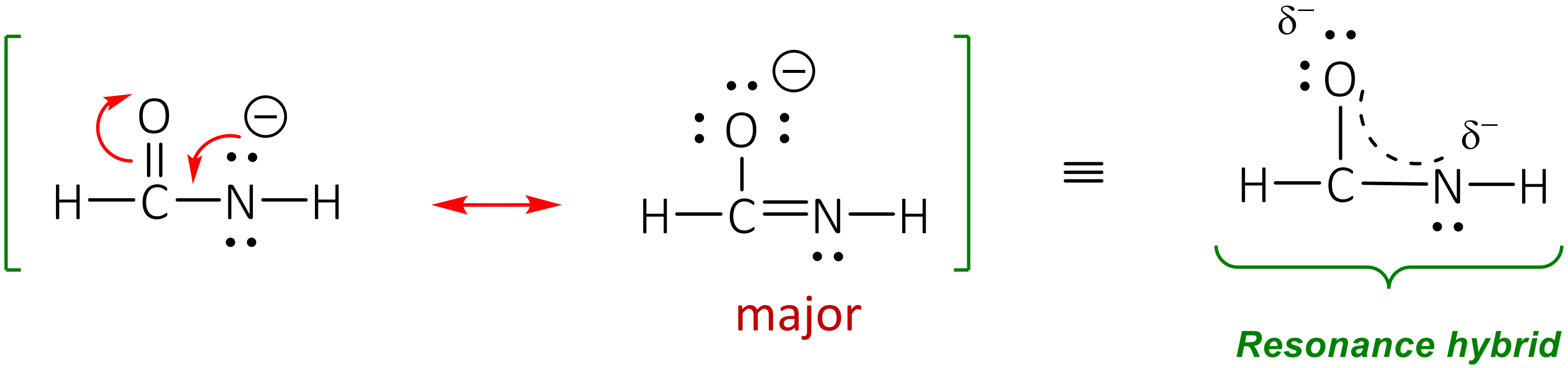


$CH_3-\overset{\oplus}{\underset{H}{C}}-CH_3$

The Resonance Hybrid

A ***resonance hybrid*** is a composite of all possible resonance structures.

- ☐ More stable resonance forms are closer representations of the real molecule than less stable ones.



✓ More bond

✓ negative charges on the electronegative atom

The more stable resonance form ---->> *major contributor*
less stable resonance form ---->> minor contributors

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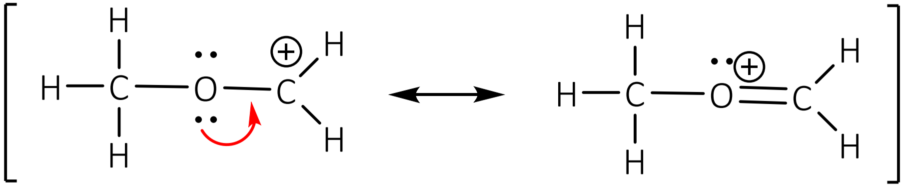
The Resonance Hybrid

Resonance form can be compared using the following criteria:

1) **More bond** : A “better” resonance structure is one that has more bonds.
2) **Any negative charges on the electronegative atom**
3) **fewer charges:** Charge separation decreases stability.

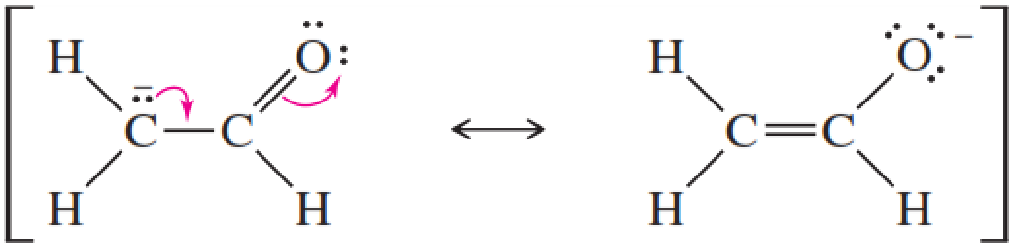


(minor contributor)

(major contributor)

more bond

The Resonance Hybrid



minor contributor

major contributor

Any negative charges on the electronegative atom

X

more bonds
fewer charges

major contributor

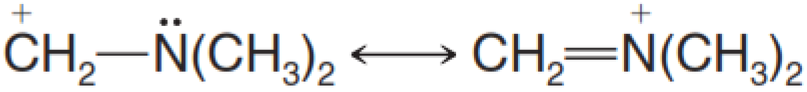
Y

minor contributor

Sample Problem 1.17

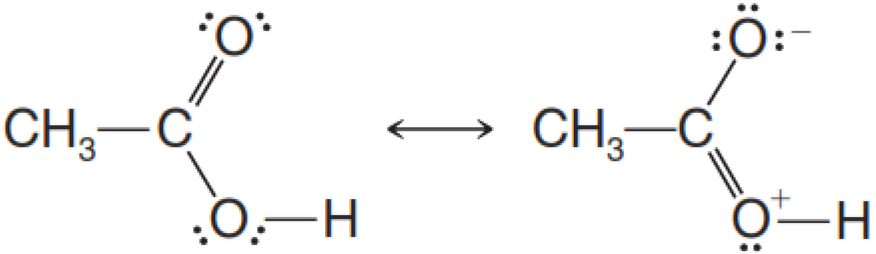
Question: From each set of resonance structures that follow, designate the one that would contribute most to the hybrid and explain your choice

(a)

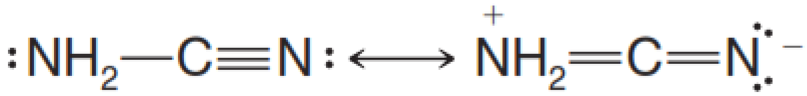


$\overset{+}{C}H_2-\ddot{N}(CH_3)_2 \longleftrightarrow CH_2=\overset{+}{N}(CH_3)_2$

(b)

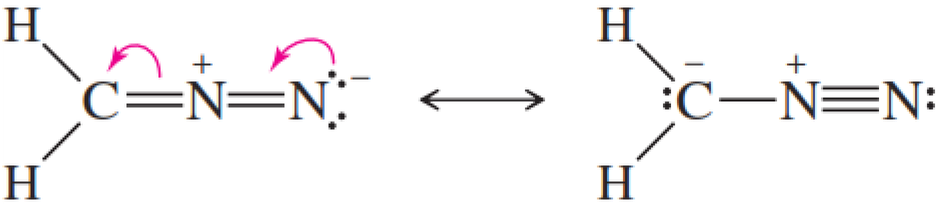


(c)



$:NH_2-C\equiv N: \longleftrightarrow \overset{+}{N}H_2=C=\ddot{N}:^{-}$

(d)



Acids and Bases

in organic compounds

Acid-Base definition

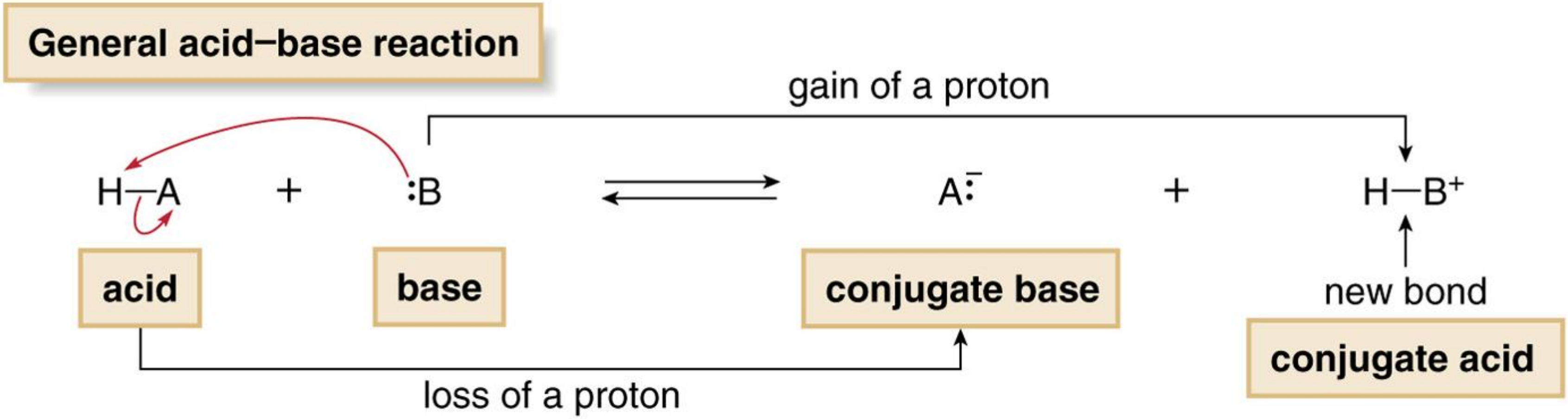
1.1) **Brønsted–Lowry:** Acids are proton (H^+) donors,
bases are proton acceptors.

1.2) A ***Lewis acid*** is a substance that can accept a pair of electrons

A ***Lewis base*** is a substance that can donate a pair of electrons

Reactions of Brønsted–Lowry Acids and Bases

- A Brønsted–Lowry acid-base reaction results in the transfer of a proton from an **acid to a base**.
- The electron pair of the base **B:** forms a new bond with the proton of the acid forming the conjugate acid of the base.
- The acid H–A loses a proton, leaving the electron pair in the H–A bond on A. This forms the conjugate base of the acid.



Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Reactions of Brønsted–Lowry Acids and Bases

- The movement of electrons in reactions can be illustrated using curved arrow notation.

- Because two electron pairs are involved in this reaction, two curved arrows are needed.

- A double reaction arrow (indicating equilibrium) is used between starting materials and products to indicate that the reaction can proceed in the forward and reverse directions.

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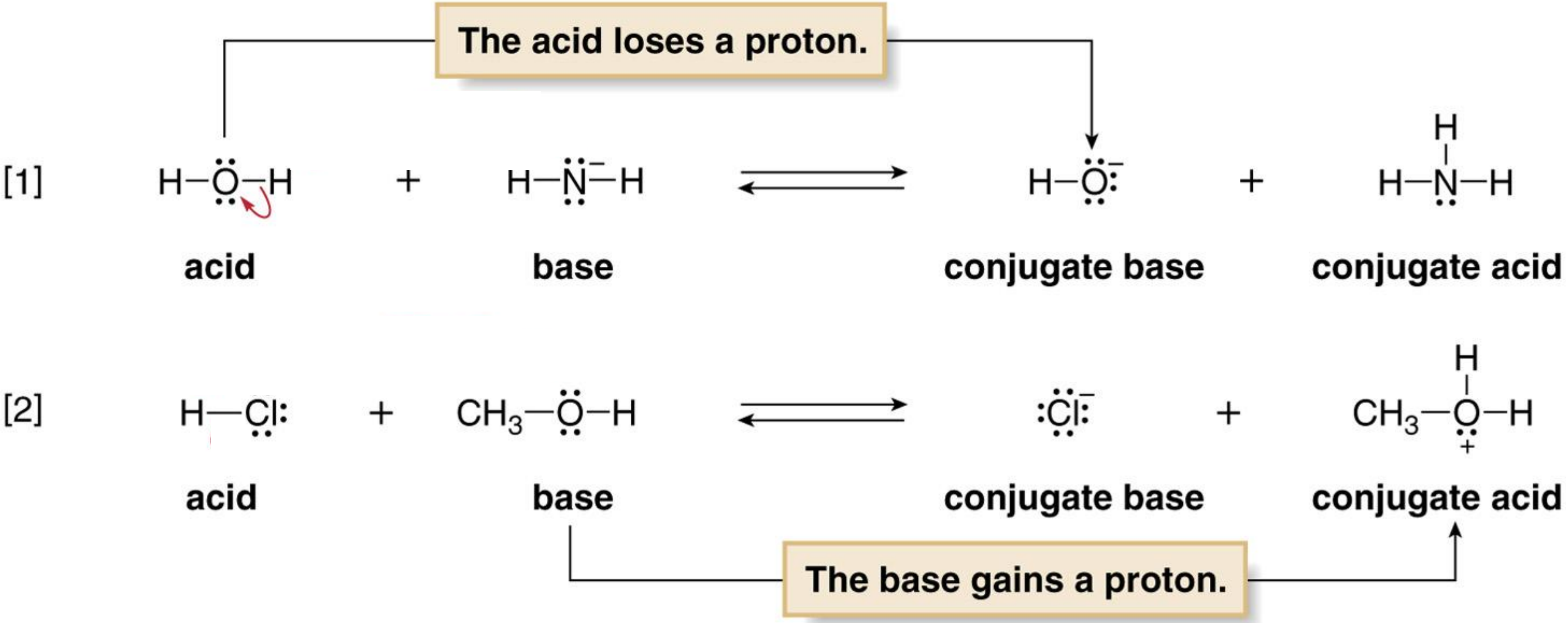
Examples of Brønsted–Lowry Acid–Base Reactions



The acid loses a proton.

$$[1]\quad \text{H–}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{–H} + \text{H–}\ddot{\underset{\cdot\cdot}{\text{N}}}^{-}\text{–H} \rightleftharpoons \text{H–}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{:}^{-} + \text{H–}\overset{\text{H}}{\underset{\cdot\cdot}{\text{N}}}\text{–H}$$

$$[2]\quad \text{H–}\ddot{\underset{\cdot\cdot}{\text{Cl}}}\text{:} + \text{CH}_3\text{–}\ddot{\underset{\cdot\cdot}{\text{O}}}\text{–H} \rightleftharpoons \text{:}\ddot{\underset{\cdot\cdot}{\text{Cl}}}\text{:}^{-} + \text{CH}_3\text{–}\overset{\text{H}}{\underset{\cdot\cdot}{\text{O}}}^{+}\text{–H}$$

The base gains a proton.

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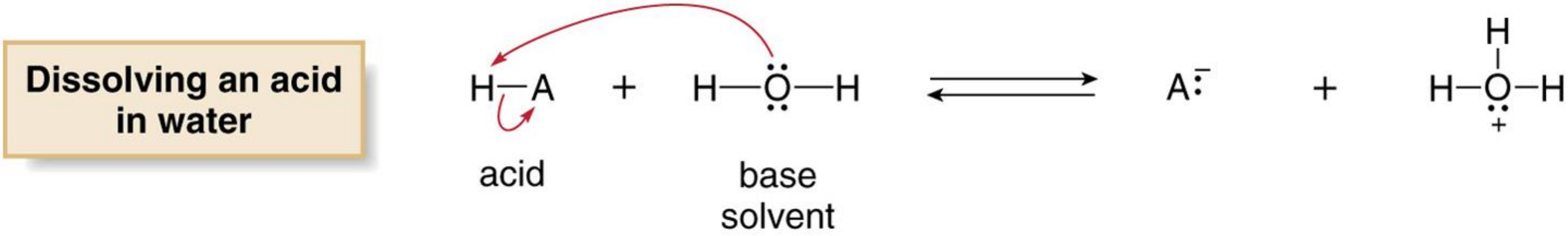
Acid Strength and pK_a

- ☐ Acid strength is the tendency of **an acid to donate a proton**.
- ☐ The more readily a **compound donates a proton, the stronger the acid.**



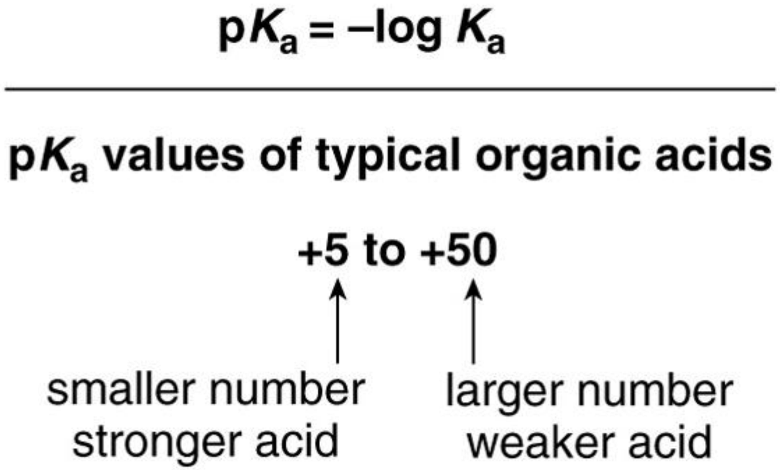
Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Acid Strength and pK_a

- It is generally more convenient when describing acid strength to use “pK_a” values than K_a values.

Definition: pK_a = −log K_a

pKa มาก เป็นกรด น้อย pKa น้อย เป็นกรด มาก



$$pK_a = -\log K_a$$

pK_a values of typical organic acids

+5 to +50

$$K_{eq} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[H_3O^+][A:^-]}{[H{-}A][H_2O]}$$

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Factors

that Determine Acid Strength

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Factors that Determine Acid Strength

- Anything that stabilizes a conjugate base A:$^-$ makes the starting acid H–A more acidic.

- **Four factors** affect the acidity of H–A. They are:
  - (I) Element effects
  - (II) Inductive effects
  - **(III) Resonance effects**
  - (IV) Hybridization effects

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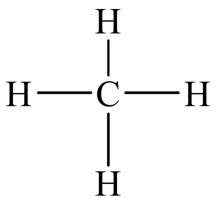
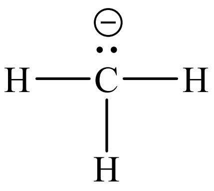
Comparing the Acidity of Any Two Acids

- Always draw the conjugate bases.
- Determine which conjugate base is more stable.
- The more stable the conjugate base, the more acidic the acid.

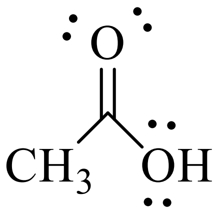
conjugate bases = species ที่มี H น้อยกว่า 1 ตัว

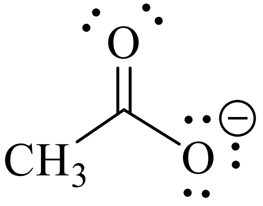
conjugate acid = species ที่มี H มากกว่า 1 ตัว





conjugate base





conjugate base

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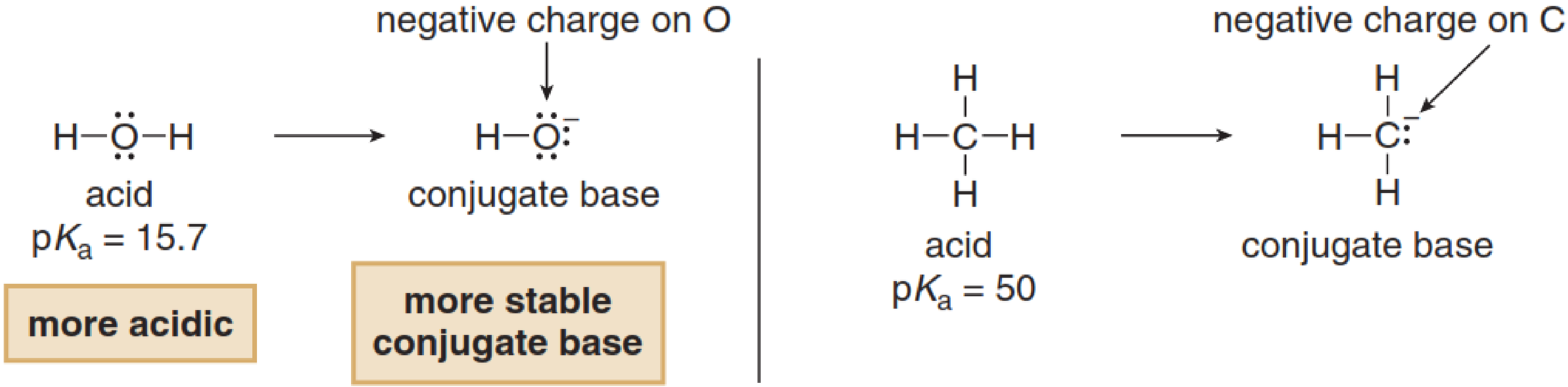
(I) Element Effects—Trends in the Periodic Table

IA) Comparing Elements in the Same Row of the Periodic Table



Oxygen atom is much **more electronegative** than carbon, oxygen more readily accepts a negative charge, making ^{-}OH much more stable than CH_3^-

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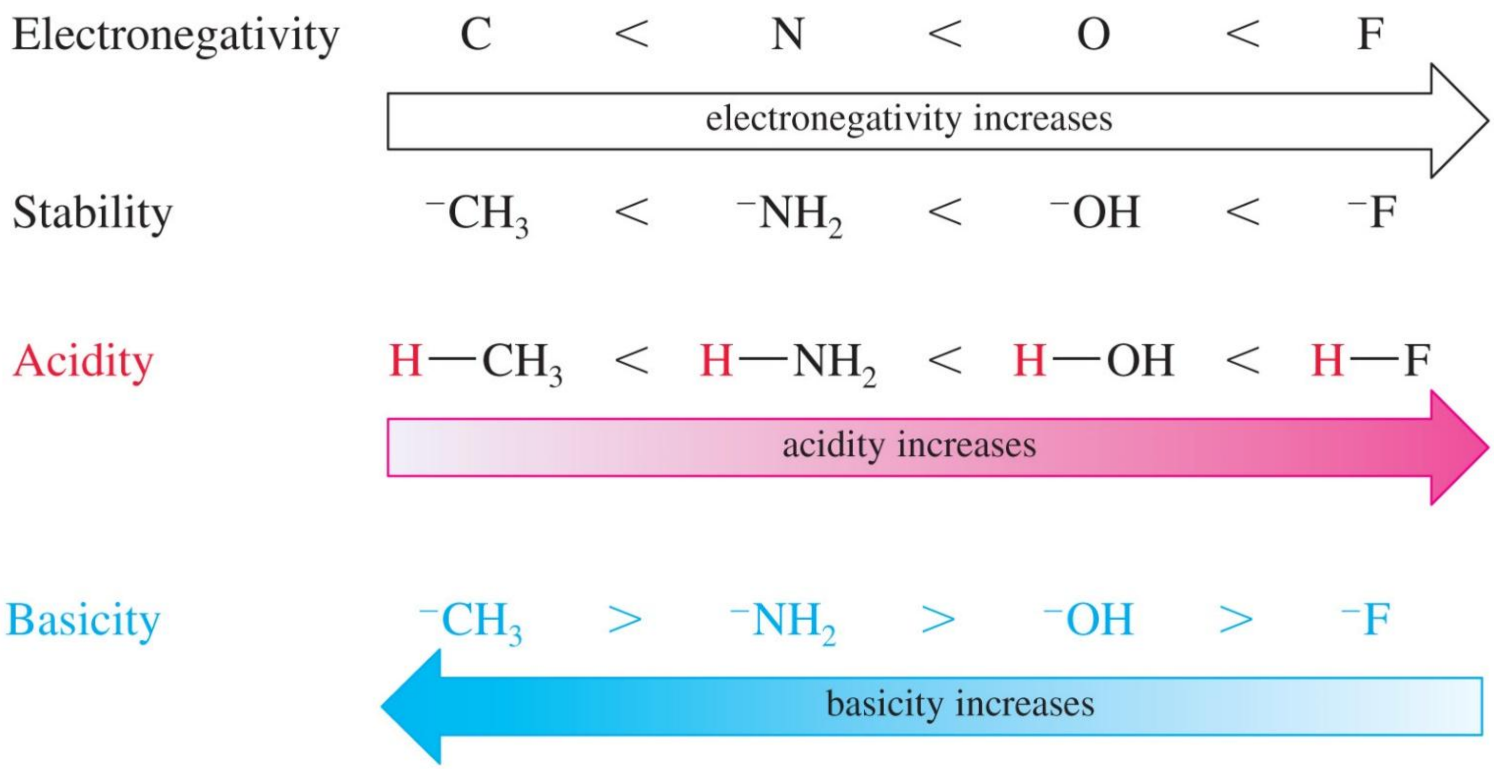
(I) Element Effects—Trends in the Periodic Table

IA) Comparing Elements in the Same Row of the Periodic Table



Electronegativity $C < N < O < F$

electronegativity increases

Stability ${}^{-}CH_3 < {}^{-}NH_2 < {}^{-}OH < {}^{-}F$

Acidity $H{-}CH_3 < H{-}NH_2 < H{-}OH < H{-}F$

acidity increases

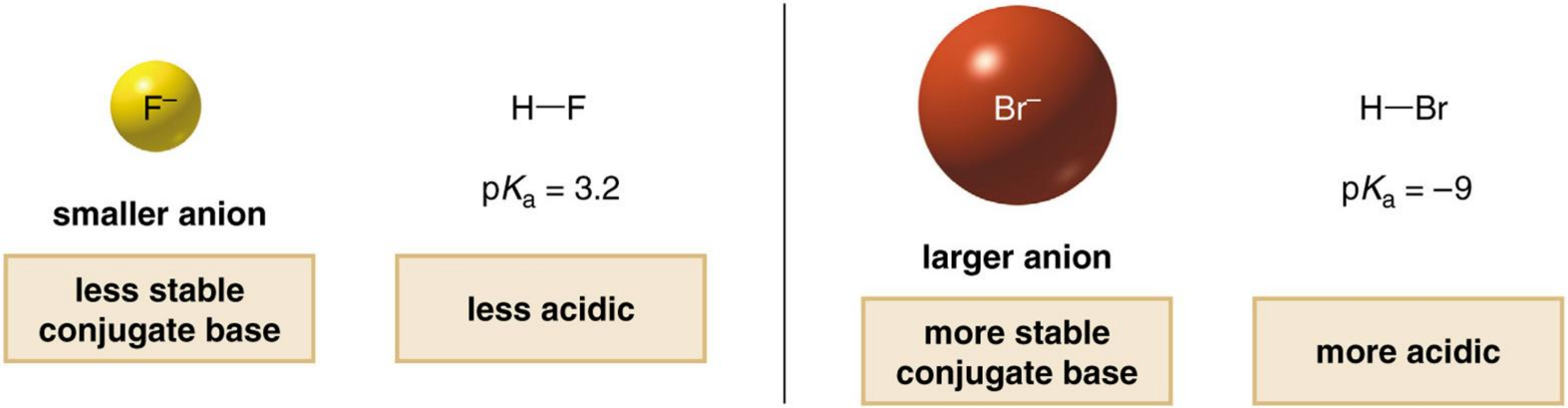
Basicity ${}^{-}CH_3 > {}^{-}NH_2 > {}^{-}OH > {}^{-}F$

basicity increases

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

(I) Element Effects—Trends in the Periodic Table

IB) Comparing Elements Down a Column of the Periodic Table



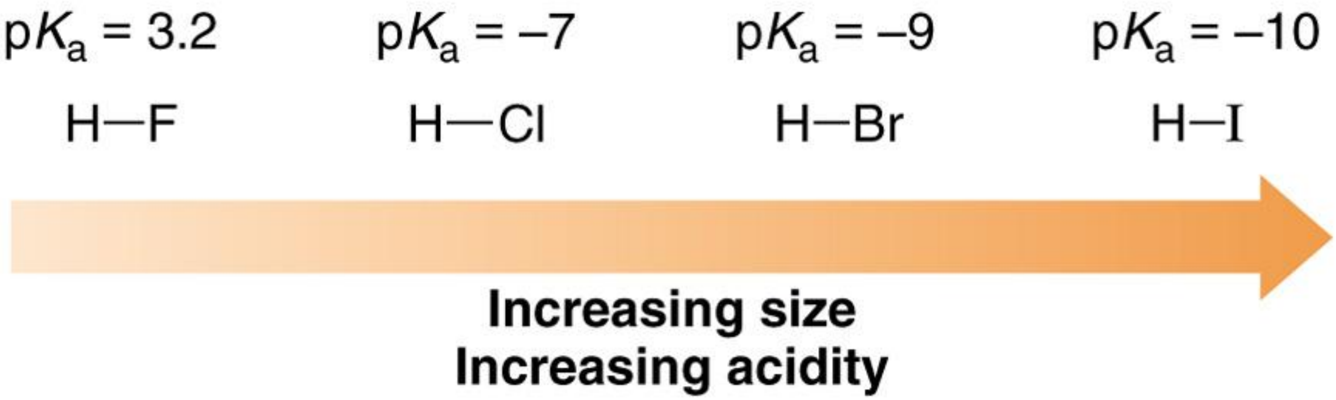
Positive or negative charge is stabilized when it is spread across a larger volume.

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

(I) Element Effects—Trends in the Periodic Table

IB) Comparing Elements Down a Column of the Periodic Table

- ☐ Down a column of the periodic table, size, and not electronegativity, determines acidity.
- ☐ The acidity of H–A increases as the size of A increases.



$pK_a = 3.2$	$pK_a = -7$	$pK_a = -9$	$pK_a = -10$
H—F	H—Cl	H—Br	H—I

Increasing size
Increasing acidity

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

Problem 1 | Without reference to a pK_a table, decide which compound in each pair is the stronger acid:

a. H_2O or HF b. H_2S or H_2O

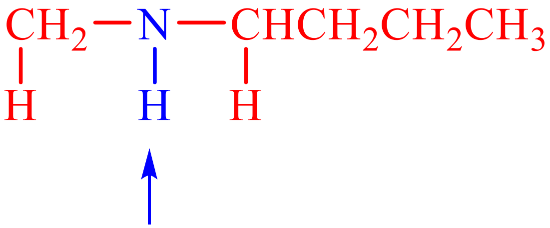
Problem 2 | Which compound in each pair of isomers is the stronger acid?

a. $CH_3CH_2CH_2NH_2$ or $(CH_3)_3N$ b. $CH_3CH_2OCH_3$ or $CH_3CH_2CH_2OH$

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

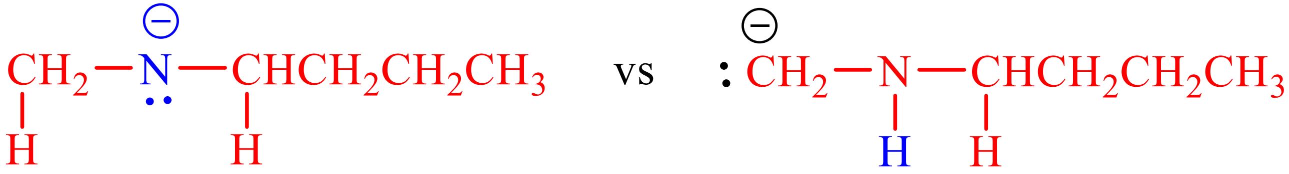
(I) Element Effects—Trends in the Periodic Table

To decide which hydrogen is most acidic, **first determine what element each hydrogen is bonded** to and then decide its acidity based on periodic trends.



$$\underset{\displaystyle H}{\underset{|}{CH_2}}-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_2CH_3$$

most acidic



$$\underset{\displaystyle H}{\underset{|}{CH_2}}-\overset{\ominus}{\underset{\cdot\cdot}{N}}-\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_2CH_3 \quad \text{vs} \quad \overset{\ominus}{:}\,CH_2-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_2CH_3$$

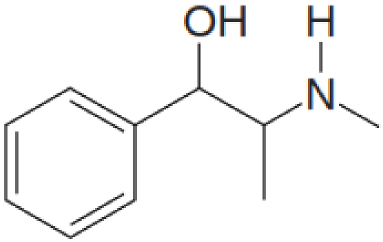
Nitrogen atom is much more electronegative than carbon, oxygen more readily accepts a negative charge

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

Problem | Which hydrogen in each molecule is most acidic?

(a) $CH_3CH_2CH_2CH_2OH$

(b)



pseudoephedrine

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

(II) Inductive Effects

An **inductive effect** is the pull of electron density through σ bonds caused by electronegativity differences of atoms.

- ❑ More **electronegative atoms stabilize regions of high electron density** by an electron withdrawing inductive effect.

$CH_3CH_2O{-}H$

ethanol

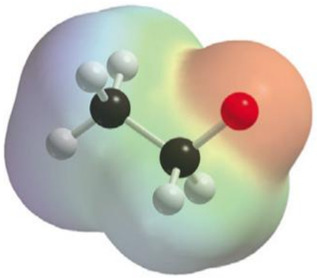
pK_a = 16

$CF_3CH_2O{-}H$

2,2,2-trifluoroethanol

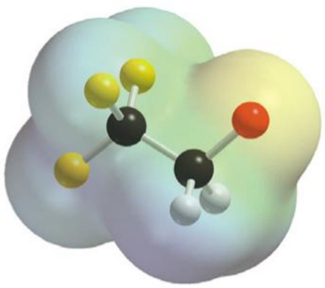
pK_a = 12.4 ← **stronger acid**

$CH_3CH_2O^-$



The dark red of the O atom indicates a region of high electron density.

$CF_3CH_2O^-$



The O atom is yellow, indicating it is less electron rich.

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

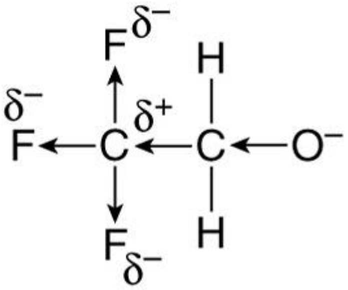
(II) Inductive Effects

Rationale for Inductive Effects

- The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.

$CH_3CH_2O^-$

No additional electronegative atoms stabilize the conjugate base.



CF_3 withdraws electron density, stabilizing the conjugate base.

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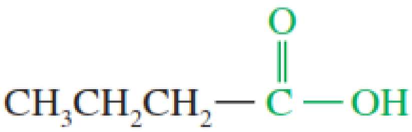
(II) Inductive Effects

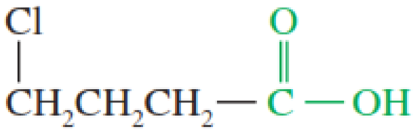
- ☐ The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- ☐ The acidity of H–A increases with the presence of electron withdrawing groups in A.



$CH_3CH_2CH_2-\overset{O}{\overset{\parallel}{C}}-OH$

butanoic acid

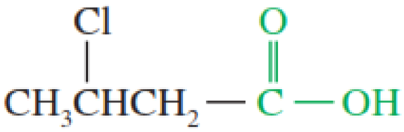
$pK_a = 4.82$



$\overset{Cl}{\overset{|}{C}}H_2CH_2CH_2-\overset{O}{\overset{\parallel}{C}}-OH$

4-chlorobutanoic acid

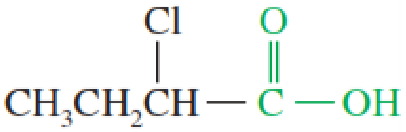
$pK_a = 4.52$



$CH_3\overset{Cl}{\overset{|}{C}}HCH_2-\overset{O}{\overset{\parallel}{C}}-OH$

3-chlorobutanoic acid

$pK_a = 4.05$

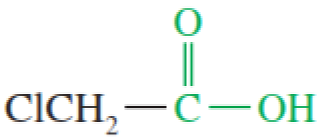


$CH_3CH_2\overset{Cl}{\overset{|}{C}}H-\overset{O}{\overset{\parallel}{C}}-OH$

2-chlorobutanoic acid

$pK_a = 2.86$

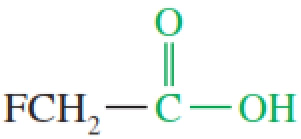
Increasing acidity



$ClCH_2-\overset{O}{\overset{\parallel}{C}}-OH$

chloroacetic acid

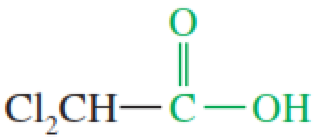
$pKa = 2.86$



$FCH_2-\overset{O}{\overset{\parallel}{C}}-OH$

fluoroacetic acid

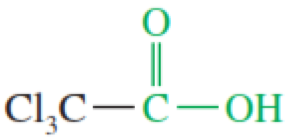
$pKa = 2.59$



$Cl_2CH-\overset{O}{\overset{\parallel}{C}}-OH$

dichloroacetic acid

$pKa = 1.26$



$Cl_3C-\overset{O}{\overset{\parallel}{C}}-OH$

trichloroacetic acid

$pKa = 0.64$

Problem | พิจารณาสารในแต่ละคู่ แล้วระบุว่าสารใดเป็นกรดที่แรงกว่ากัน พร้อมระบุเหตุผลพอสังเขป

(a) Cl_2CHCH_2OH กับ $Cl_2CHCH_2CH_2OH$

(b) CH_3COOH กับ NO_2CH_2COOH

Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*

(III) Resonance Effects

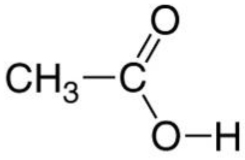
- Delocalization of charge through resonance influences acidity.

- Acetic acid is more acidic than ethanol, even though both molecules have the negative charge on the same element, O.

$CH_3CH_2O{-}H$

ethanol

$pK_a = 16$

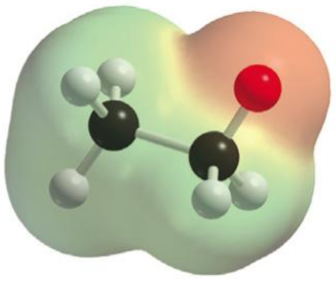


$CH_3{-}C(=O){-}O{-}H$

acetic acid

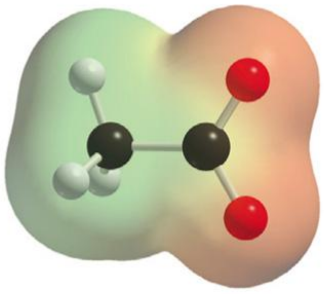
$pK_a = 4.8$ ← **stronger acid**

$CH_3CH_2O^-$



The negative charge is concentrated on the single oxygen atom, making this anion *less stable.*

CH_3COO^-

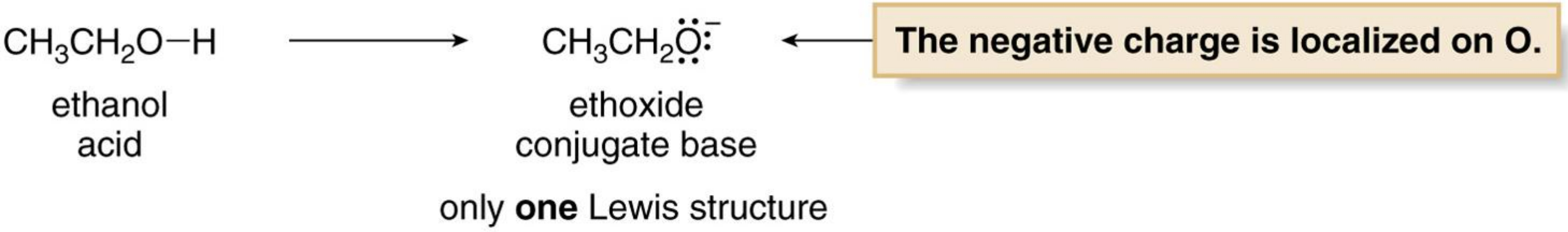


The negative charge is delocalized over both oxygen atoms, making this anion *more stable.*

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

(A) Comparison of Ethoxide and Acetate Ions

- The conjugate base of ethanol has a localized charge.



$CH_3CH_2O{-}H \longrightarrow CH_3CH_2\ddot{O}:^-$

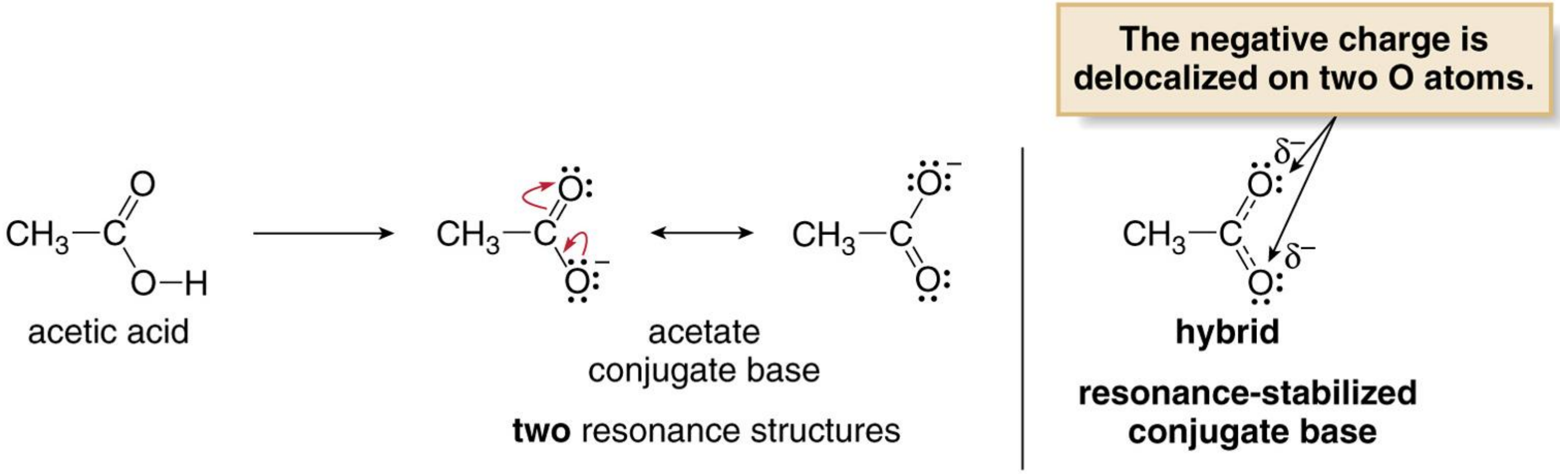
ethanol
acid

ethoxide
conjugate base

only **one** Lewis structure

The negative charge is localized on O.

- The conjugate base of acetic acid is resonance delocalized.



acetic acid

acetate
conjugate base

two resonance structures

hybrid

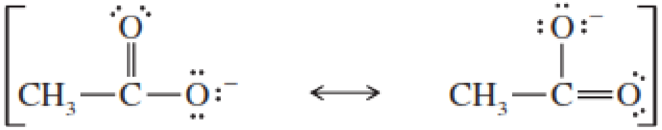
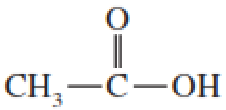
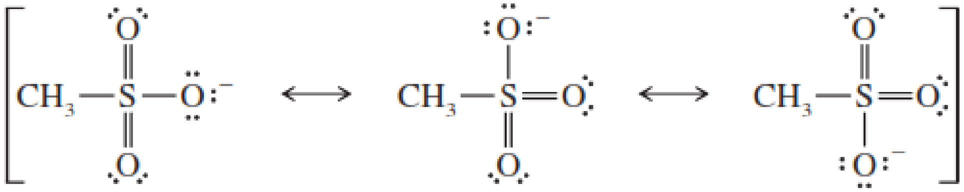
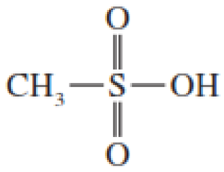
resonance-stabilized
conjugate base

The negative charge is delocalized on two O atoms.

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

(III) Resonance Effects

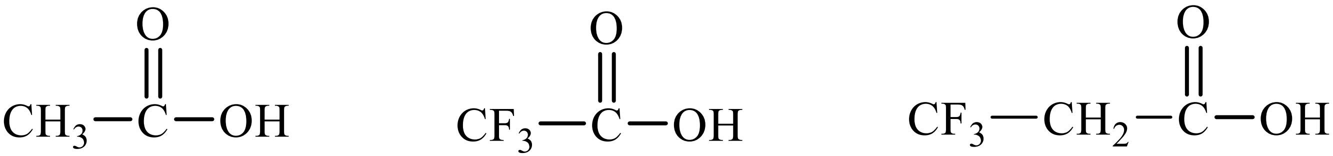
- ☐ resonance delocalization is often the dominant effect helping to stabilize an anion.
- ☐ Resonance effect มีผลมากกว่า inductive effect

Conjugate Base	Acid	pK_a
$CH_3CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{:}^-$ ethoxide ion	$CH_3CH_2{-}OH$ ethanol	15.9 (weak acid)
 acetate ion	 $CH_3{-}\overset{\overset{\displaystyle O}{\Vert}}{C}{-}OH$ acetic acid	4.74 (moderate acid)
 methanesulfonate ion	 $CH_3{-}\overset{\overset{\displaystyle O}{\Vert}}{\underset{\underset{\displaystyle O}{\Vert}}{S}}{-}OH$ methanesulfonic acid	−1.2 (strong acid)

Wade, L. G. *Organic Chemistry;* Pearson Prentice Hall, 2010.

Problem (a) Rank the conjugate bases in the order you would predict, from least stable to most stable .

(b) Rank the original compounds in order, from weakest acid to strongest acid.

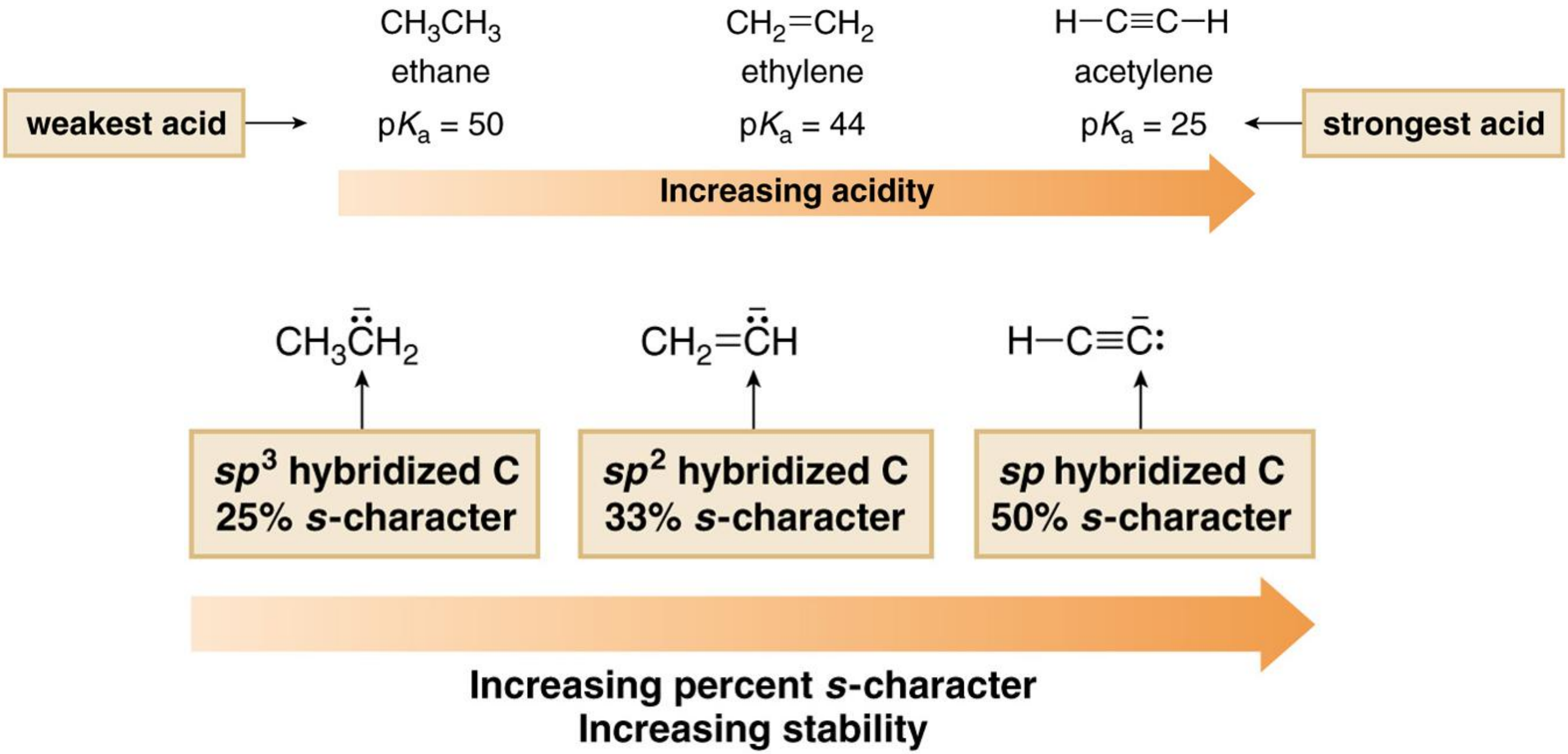


$CH_3-C(=O)-OH$ $CF_3-C(=O)-OH$ $CF_3-CH_2-C(=O)-OH$ CH_3CH_2OH

Wade, L. G. *Organic Chemistry;* Pearson Prentice Hall, 2010.

(IV) Hybridization Effects

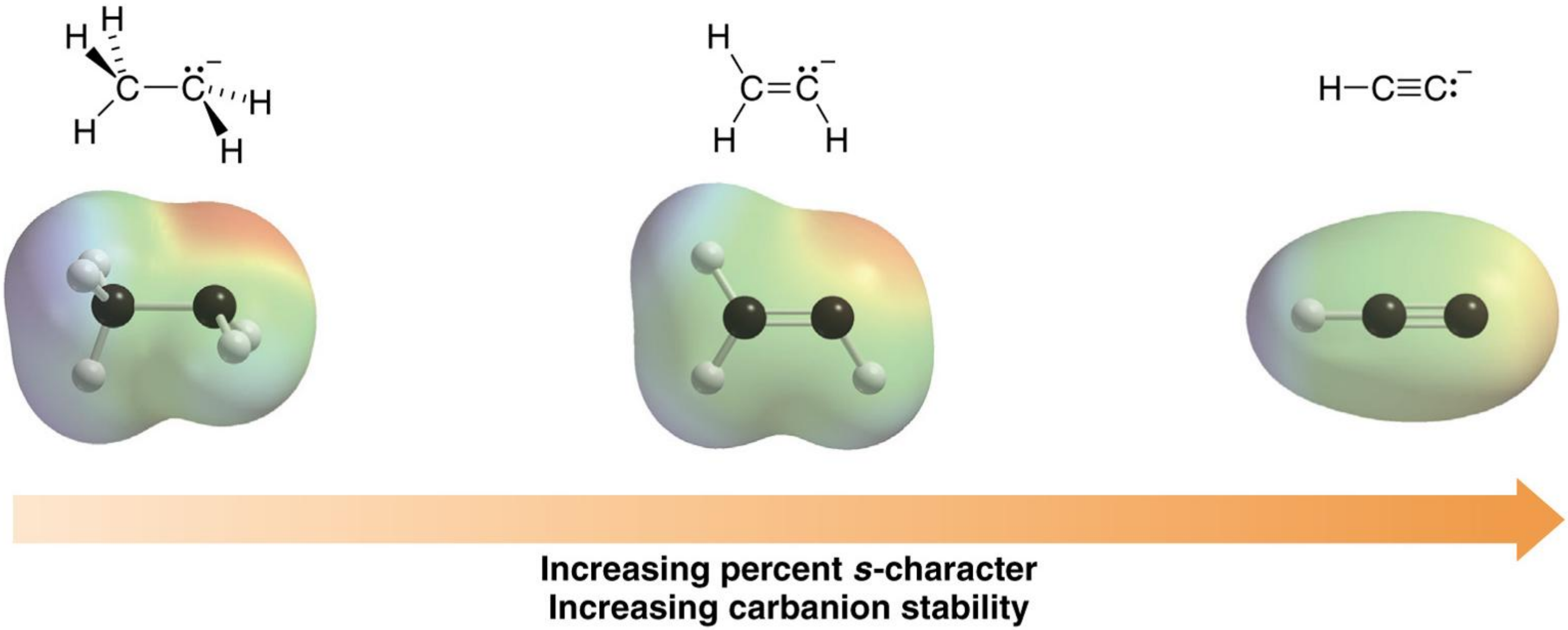
- ☐ Consider the relative acidities of three different compounds containing C–H bonds.



Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Stability of Conjugate Bases

- The higher the percent of ***s-character*** of the hybrid orbital, the more stable the conjugate base.



As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Problem | For each pair of compounds;

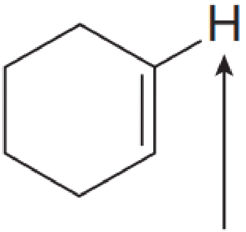
[1]Which indicated H is more acidic?

[2] Draw the conjugate base of each acid.

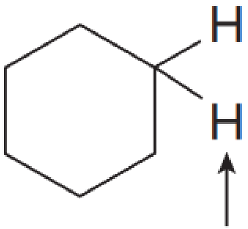
[3] Which conjugate base is stronger?

a. $CH_3CH_2{-}C{\equiv}C{-}\underset{\uparrow}{H}$ or $CH_3CH_2CH_2CH_2{-}\underset{\uparrow}{H}$

b.

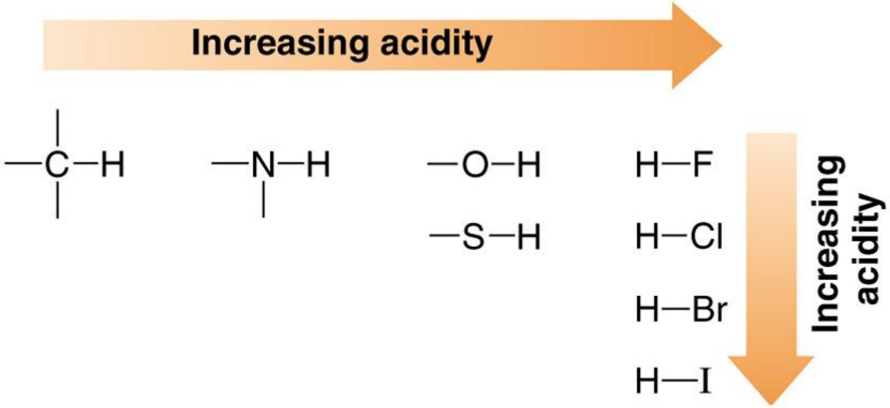


or



Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

|| Summary of Factors that Determine Acid Strength

Factor	**Example**
1. **Element effects:** The acidity of H – A increases both left-to-right across a row and down a column of the periodic table.	 **Increasing acidity** → $-\overset{\mid}{\underset{\mid}{C}}-H$ $-\underset{\mid}{N}-H$ $-O-H$ $H-F$ $-S-H$ $H-Cl$ $H-Br$ $H-I$ ↓ **Increasing acidity**
2. **Inductive effects:** The acidity of H – A increases with the presence of electron-withdrawing groups in A.	CH_3CH_2O-H CF_3CH_2O-H **more acidic**
3. **Resonance effects:** The acidity of H – A increases when the conjugate base A:⁻ is resonance stabilized.	CH_3CH_2O-H CH_3COO-H **more acidic**
4. **Hybridization effects:** The acidity of H – A increases as the percent *s*-character of A:⁻ increases.	CH_3CH_3 $CH_2{=}CH_2$ $H-C\equiv C-H$ **Increasing acidity** →

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Problem | จงทำนายว่าสารใดเป็นกรดที่แรงกว่ากัน พร้อมให้เหตุผลประกอบ

(a)

(b)

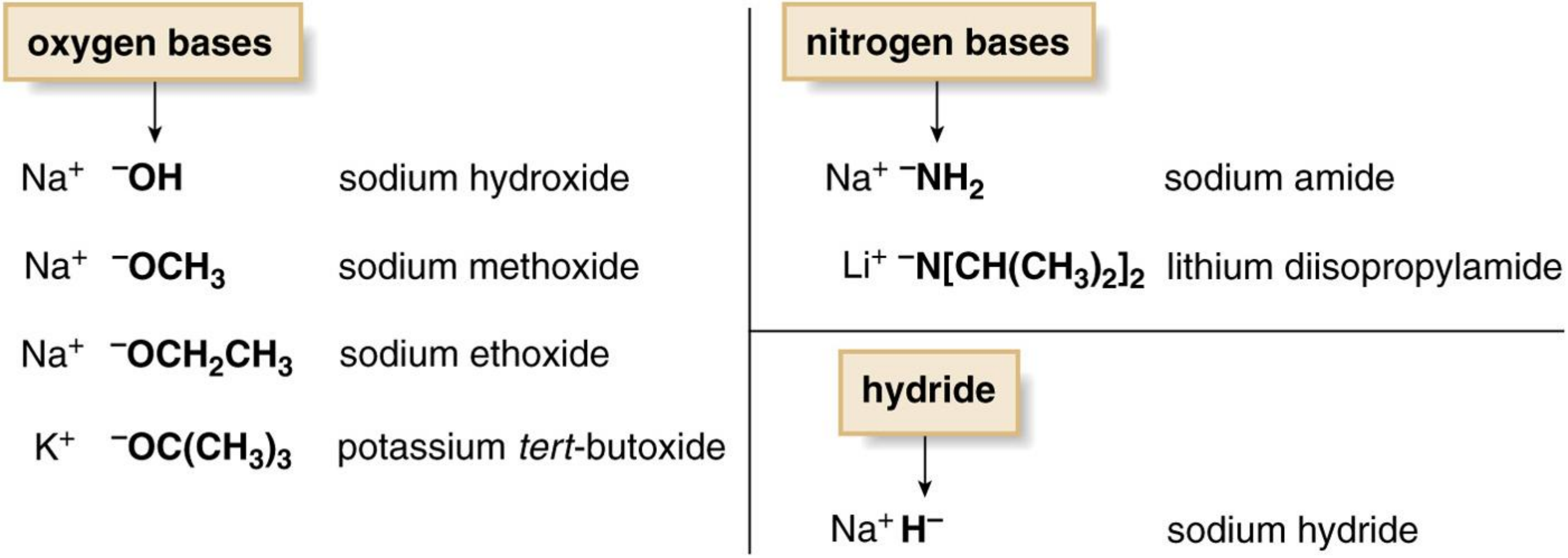
(c)

(d)

Pine, S. H. *Organic Chemistry; McGraw-Hill, 1987.*

Commonly Used Bases in Organic Chemistry

- Strong bases have a net **negative charge**, but not all negatively charged species are strong bases. For example, F^-, Cl^-, Br^-, or I^-,



oxygen bases

$Na^+\ ^-OH$	sodium hydroxide
$Na^+\ ^-OCH_3$	sodium methoxide
$Na^+\ ^-OCH_2CH_3$	sodium ethoxide
$K^+\ ^-OC(CH_3)_3$	potassium *tert*-butoxide

nitrogen bases

$Na^+\ ^-NH_2$	sodium amide
$Li^+\ ^-N[CH(CH_3)_2]_2$	lithium diisopropylamide

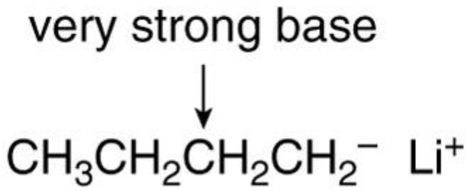
hydride

$Na^+\ H^-$	sodium hydride

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Characteristics of Strong Organic Bases

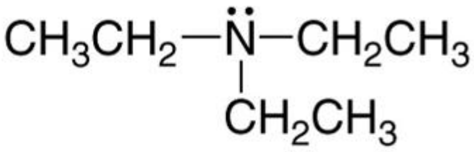
- Carbanions, negatively charged carbon atoms, are especially strong bases. A common example is butyllithium.


very strong base

$CH_3CH_2CH_2CH_2^-\ Li^+$

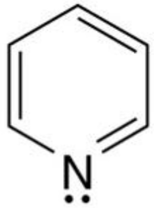
butyllithium

- Amines are organic base due to lone pair on N atom
- They are weaker bases since they are neutral, not negatively charged.



$CH_3CH_2-\ddot{N}(CH_2CH_3)-CH_2CH_3$

triethylamine



pyridine

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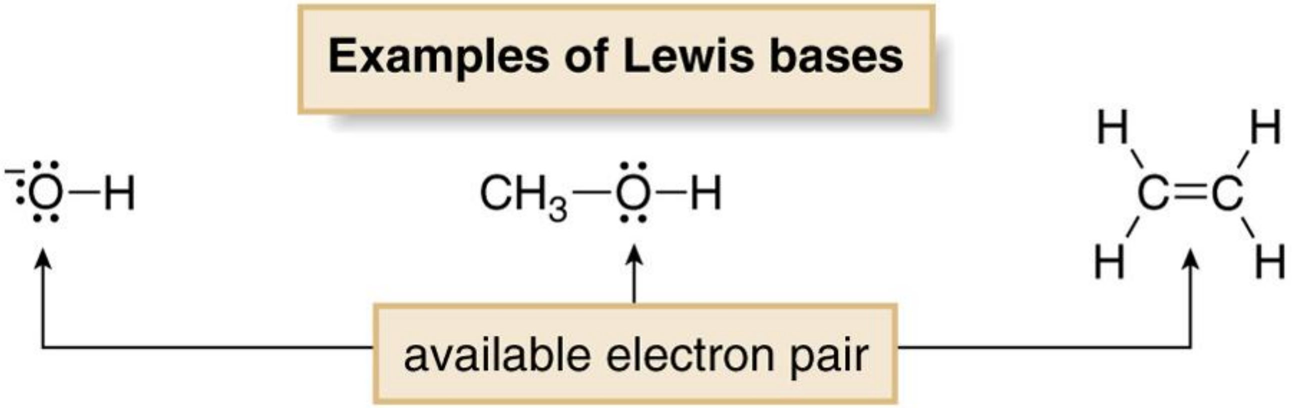
Lewis Acids and Bases

A ***Lewis acid*** is a substance that can accept a pair of electrons

A ***Lewis base*** is a substance that can donate a pair of electrons —a lone pair or an electron pair in a π bond

- Lewis base donates electron pair to anything that is electron deficient.



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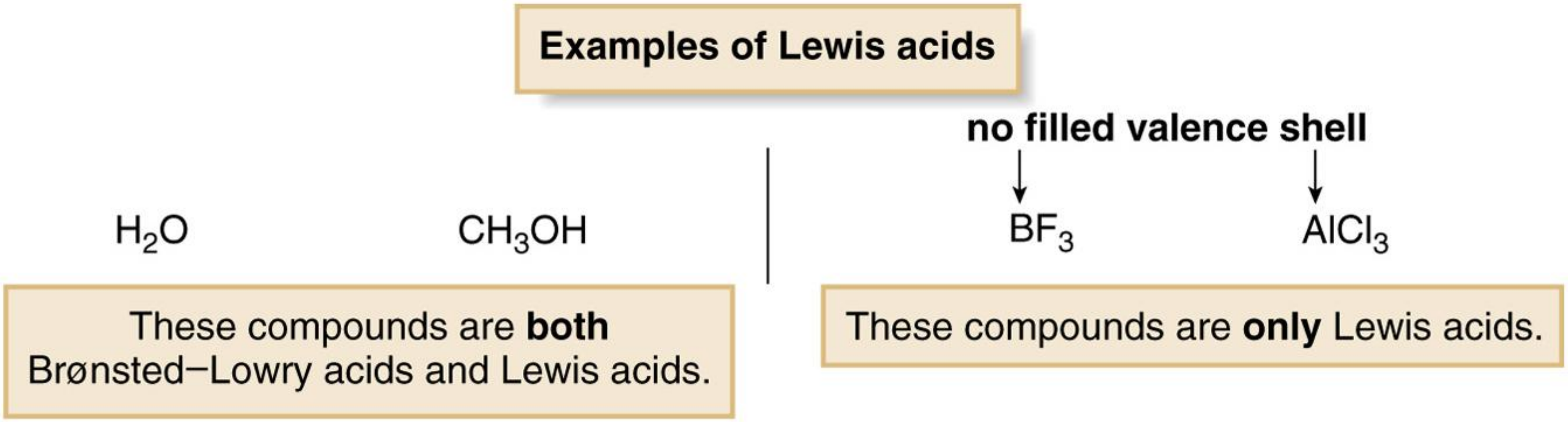
Lewis Acids

- Any species that is electron deficient and capable of accepting an electron pair is also a **Lewis acid**.
- Common examples of Lewis acids (which are not Brønsted–Lowry acids) contain elements in **group 3A** of the periodic table that can accept an electron pair because ***they do not have filled valence shells of electrons***.



Examples of Lewis acids

no filled valence shell

H_2O CH_3OH | BF_3 $AlCl_3$

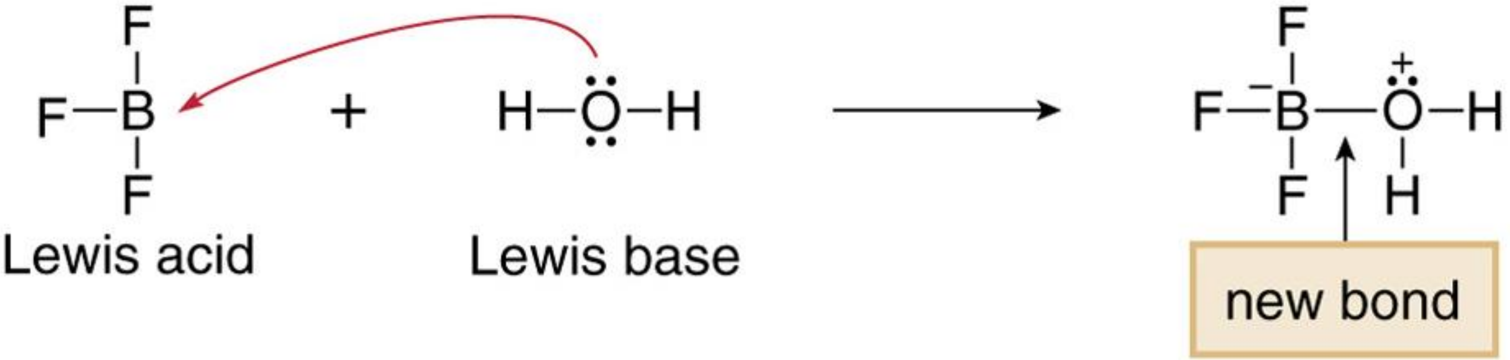
These compounds are **both** Brønsted–Lowry acids and Lewis acids.

These compounds are **only** Lewis acids.

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Lewis Acid–Base Reactions

- ☐ In a Lewis acid–base reaction, a Lewis base donates an electron pair to a Lewis acid—*using curved arrow*
- ☐ This is illustrated in the reaction of BF_3 with H_2O. H_2O donates an electron pair to BF_3 to form a new bond.



- ➢ Lewis acid–base reactions illustrate a general pattern in organic chemistry.
- ➢ Electron-rich species react with electron-poor species

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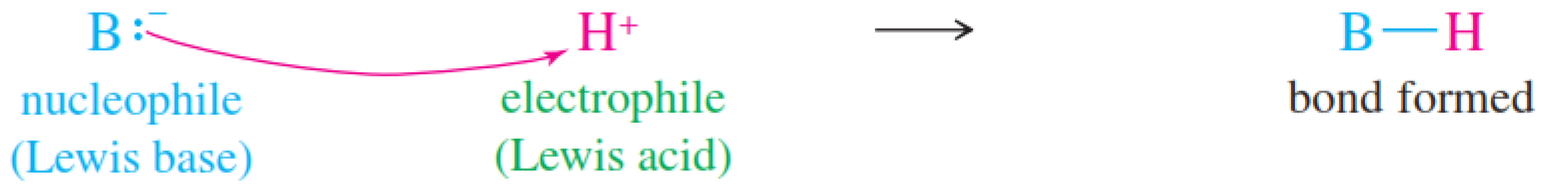
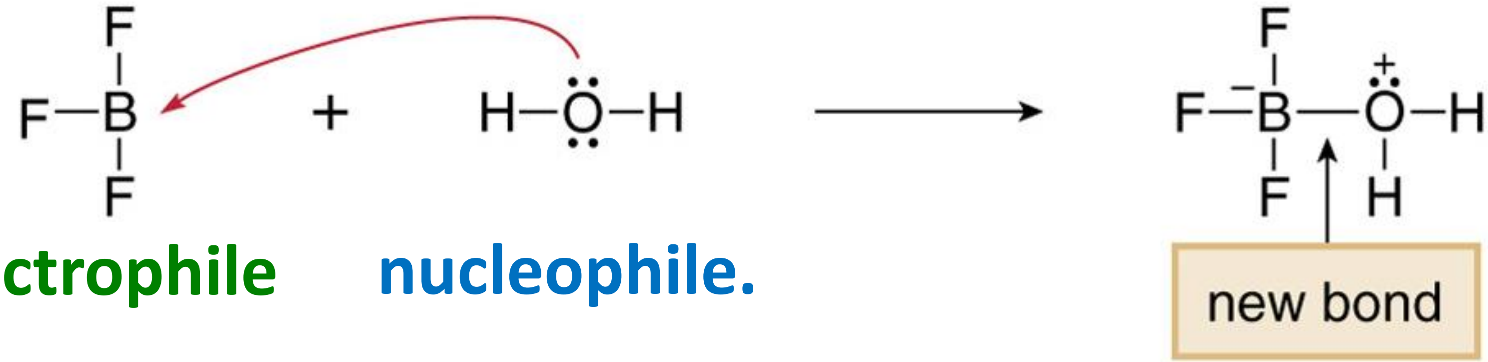
Electrophiles and Nucleophiles

- A Lewis acid is also called an **electrophile.**

Nucleophile = nucleus loving.
Electrophile = electron loving.

- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a **nucleophile.**



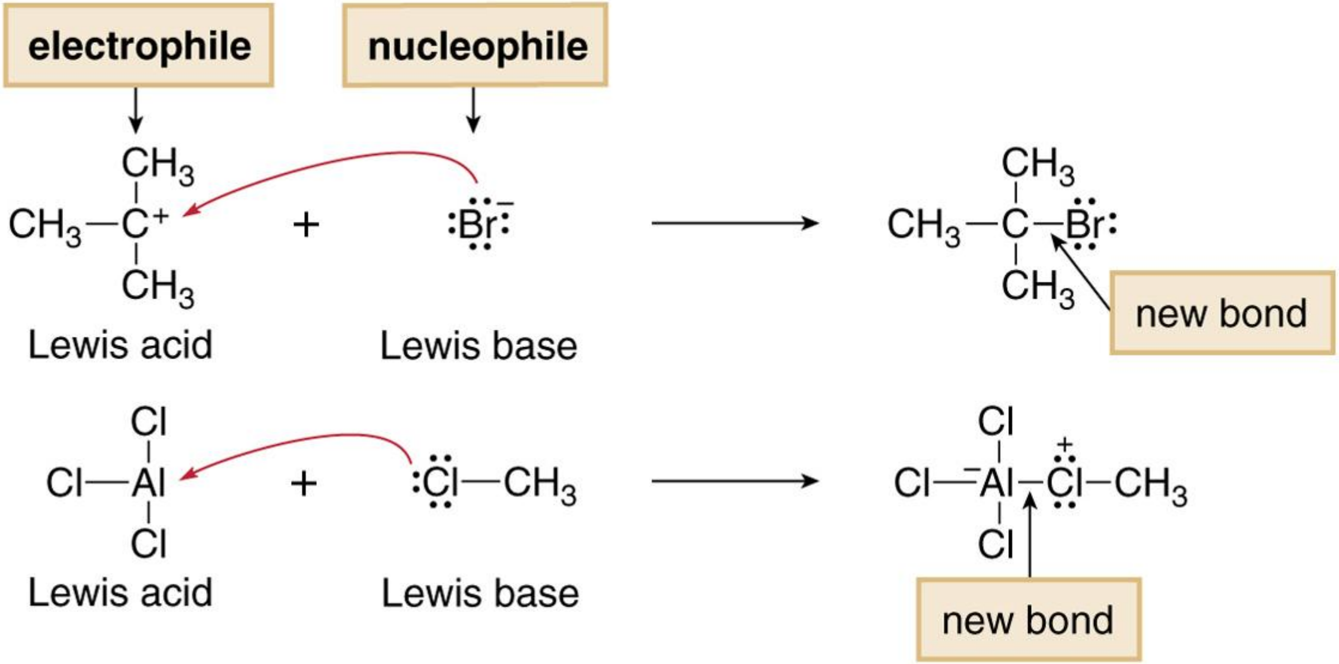


electrophile **nucleophile.**

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Lewis Acid–Base Reactions that Form One New Covalent Bond

- ❑ Note that in each reaction below, the electron pair is not removed from the Lewis base.
- ❑ Instead, it is donated to an atom of the Lewis acid and one new covalent bond is formed.



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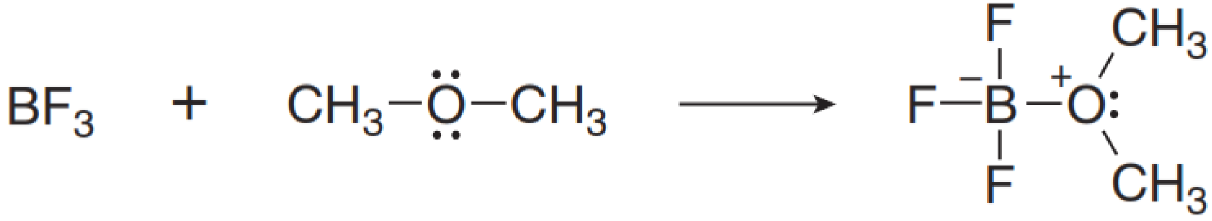
Problem 1

For each reaction, label the Nucleophile and electrophile. Use curved arrow notation to show the movement of electron pairs.

a.



$$BF_3 + CH_3-\ddot{\underset{..}{O}}-CH_3 \longrightarrow F-\overset{F}{\underset{F}{\overset{|}{\underset{|}{\overset{-}{B}}}}}-\overset{+}{O}(CH_3)_2$$

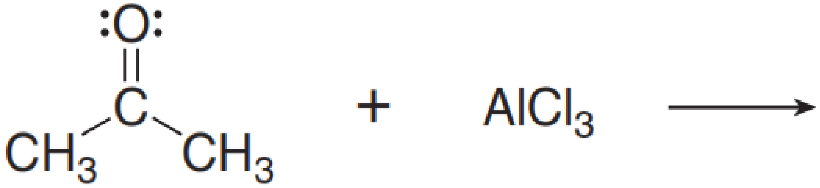
b. $(CH_3)_2\overset{+}{C}H \quad + \quad {}^{-}OH \longrightarrow (CH_3)_2CHOH$

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

Problem 2 Draw the products of each reaction, and label the nucleophile and electrophile. Use curved arrow notation to show the movement of electron pairs.

a. $CH_3CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_2CH_3 \quad + \quad BBr_3 \longrightarrow$

b.



$(CH_3)_2C=O + AlCl_3 \longrightarrow$

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

การเขียนลูกศรแสดงการเกิดปฏิกิริยาเคมี

(curved-arrow formalism)

การเขียนลูกศรแสดงการเกิดปฏิกิริยาเคมี

(curved-arrow formalism)

ลูกศรโค้ง (Curved arrows) เขาไว้ใช้ทำอะไร?

ลูกศร	ชื่อ	การใช้งาน
→	ลูกศรปฏิกิริยา	ใช้คั่นระหว่างสารตั้งต้นและสารผลิตภัณฑ์ในสมการเคมี
	ลูกศรเต็มหัว (A full-headed curved arrow)	ใช้แสดงการเคลื่อนของอิเล็กตรอน 1 คู่
	ลูกศรครึ่งหัว (A half-headed curved arrow)	ใช้แสดงการเคลื่อนของอิเล็กตรอน 1 ตัว

☐ ใช้แสดงทิศการเคลื่อนที่ของอิเล็กตรอนในกลไกของปฏิกิริยา

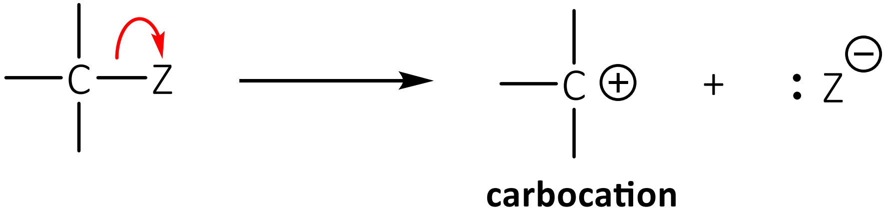
☐ การเขียนลูกศรโค้งจะใช้ในการอธิบายกลไกการเกิดปฏิกิริยาในเคมีอินทรีย์ และใช้ในการทำนายสารผลิตภัณฑ์ของปฏิกิริยาเคมีอินทรีย์

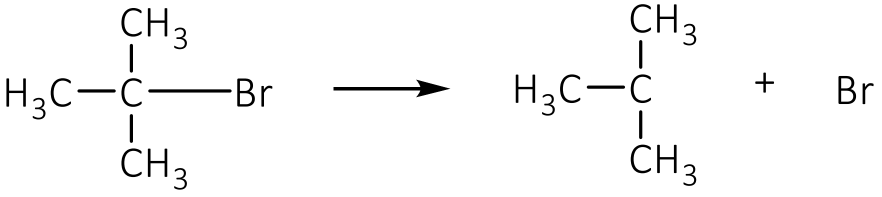
Solomons, T. W. Graham, Fryhle, Craig B., Snyder, Scott A.. (2014). *Organic Chemistry* (11th ed.). Singapore: John Wiley & Sons.

พื้นฐานการสร้าง และการสลายพันธะ

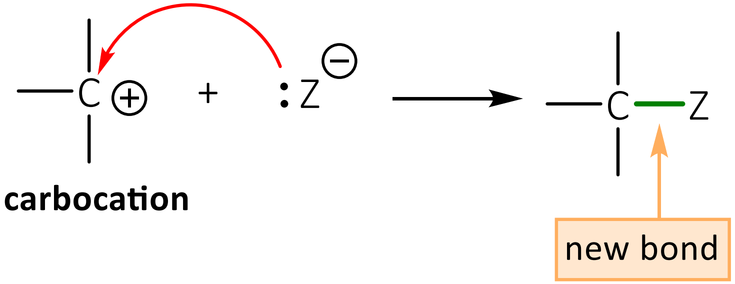
(curved-arrow formalism)

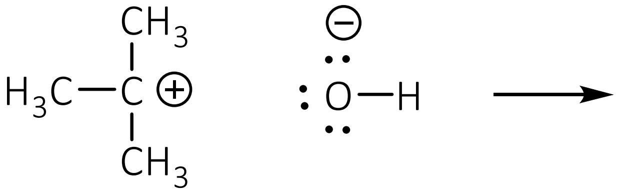
Heterolytic cleavage





Forming a bond from two ions



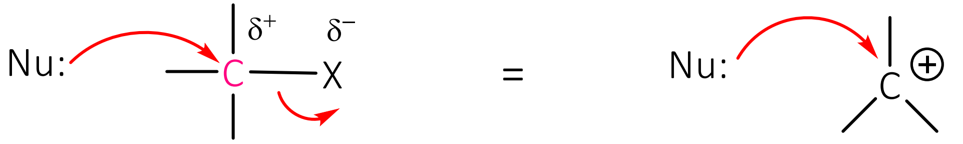


Solomons, T. W. Graham, Fryhle, Craig B., Snyder, Scott A.. (2014). *Organic Chemistry* (11th ed.). Singapore: John Wiley & Sons.

รูปแบบการเขียนลูกศรแสดงการเกิดปฏิกิริยาเคมี

(curved-arrow formalism)

แบบที่ 1

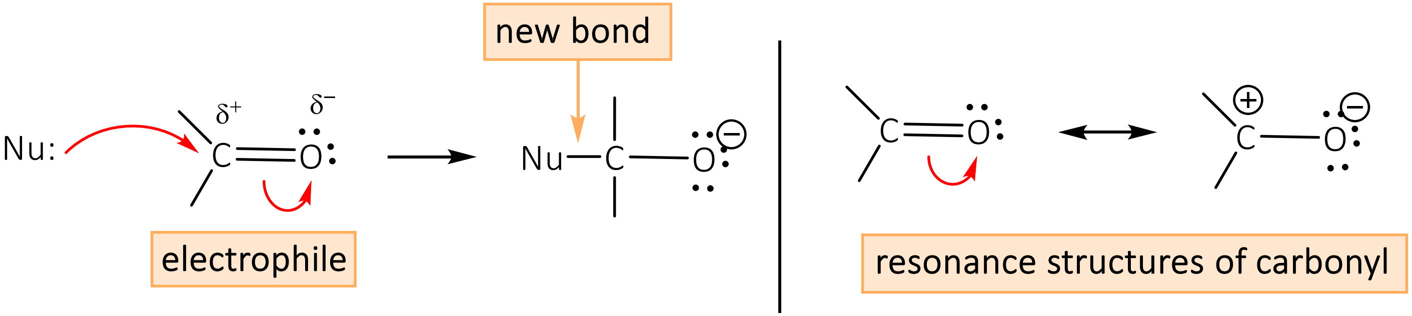


(X = Cl, Br, I)

electrophile

electrophile

แบบที่ 2

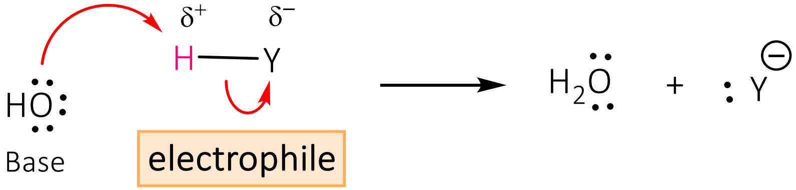


new bond

electrophile

resonance structures of carbonyl

แบบที่ 3



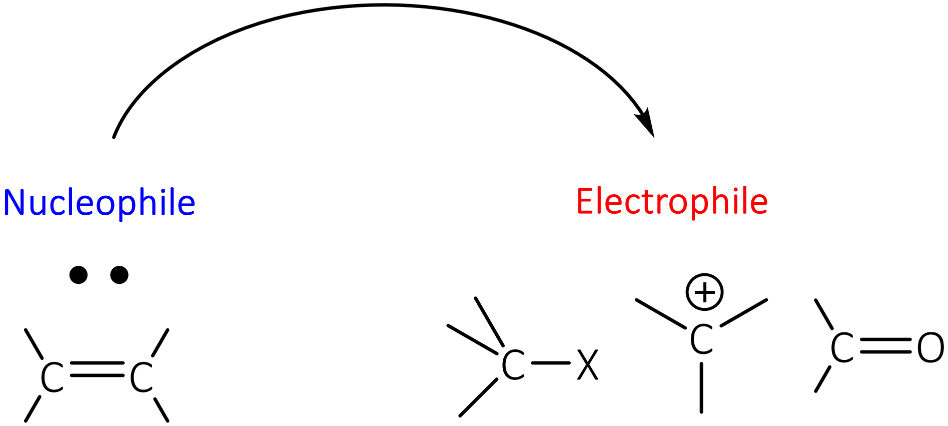
electrophile

(Y = F, O, Cl, Br)

Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.

หลักการเขียนลูกศรแสดงการเกิดปฏิกิริยา

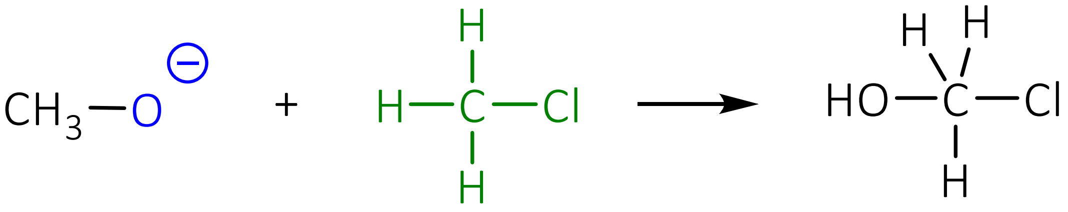
1. พิจารณาเติม lone paired electrons ให้ครบตามกฎออกเตต กับอะตอมที่ไม่ใช่ C กับ H (heteroatom)
2. ระบุว่าสารตัวไหนเป็น nucleophiles ตัวไหนเป็น electrophiles
3. **ลูกศรเริ่มจากไหนไปไหน**: หางลูกศรเริ่มจาก nucleophile (อิเล็กตรอนคู่โดดเดี่ยว, ประจุลบ, พันธะคู่) ลากหัวลูกศรชี้ไปที่ตัว electrophile



Solomons, T. W. Graham, Fryhle, Craig B., Snyder, Scott A.. (2014). *Organic Chemistry* (11th ed.). Singapore: John Wiley & Sons.

หลักการเขียนลูกศรแสดงการเกิดปฏิกิริยา

4. ลูกศรที่เขียนไปชนอิเล็กโทรไฟล์ คือ การสร้างพันธะใหม่ขึ้น ถ้ามีการสร้างพันธะใหม่เกิดขึ้นจะทำให้คาร์บอนอะตอมมีแขนเกิน 4 แขนไหม จึงต้องเขียนลูกศรเพื่อทำลายพันธะ

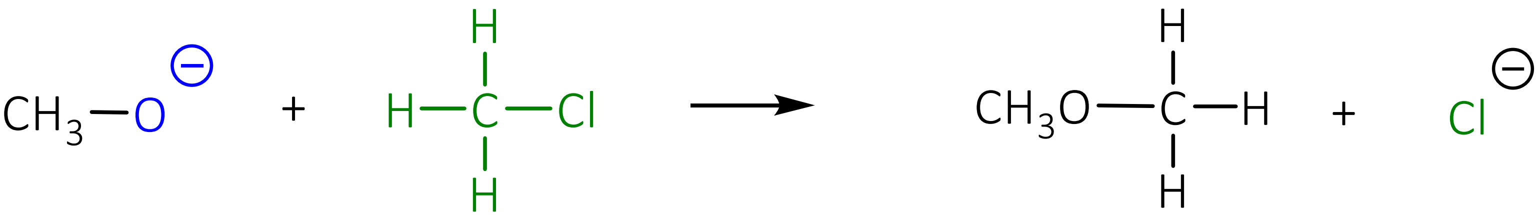


C แขนเกิน ต้องทำยังไงนะ

5. ตรวจสอบสุดท้ายว่า ผลรวมของ formal charge ของแต่ละฝั่งเท่ากันหรือไม่ หากไม่เท่าให้หาอะตอมที่มีจำนวนพันธะไม่ปกติ (O =2 bonds, C = 4 bonds, หมู่ 7 = 1 พันธะ) แล้ว assign formal charge ให้ถูกต้อง

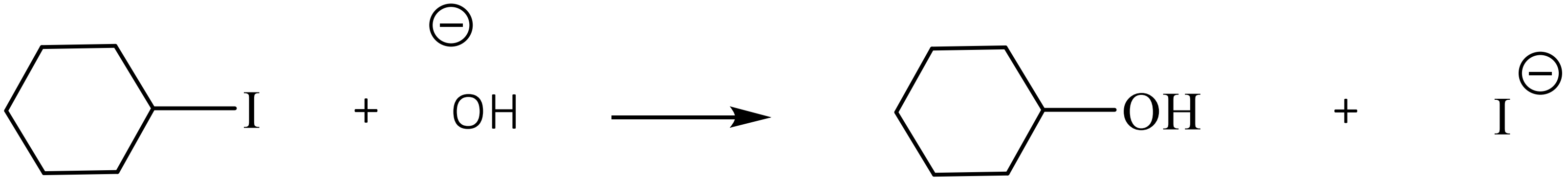
Solomons, T. W. Graham, Fryhle, Craig B., Snyder, Scott A.. (2014). *Organic Chemistry* (11th ed.). Singapore: John Wiley & Sons.

Example 1A

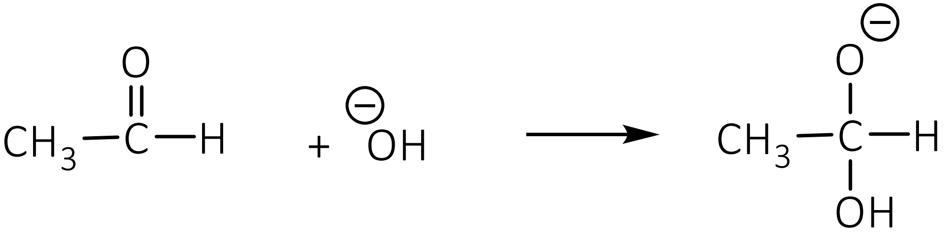


$$CH_3{-}O^{\ominus} + H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}Cl \longrightarrow CH_3O{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}H + Cl^{\ominus}$$

Example 1B

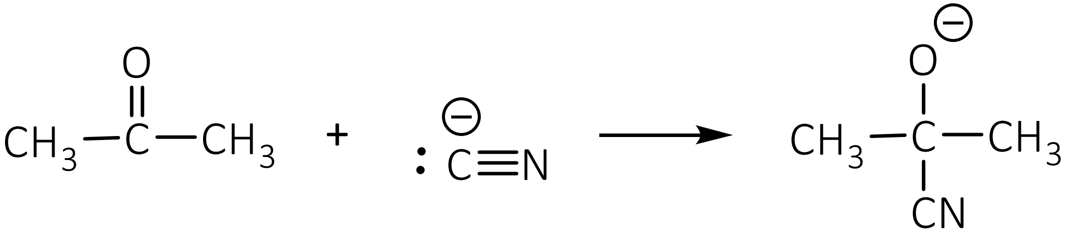


Example 2A |

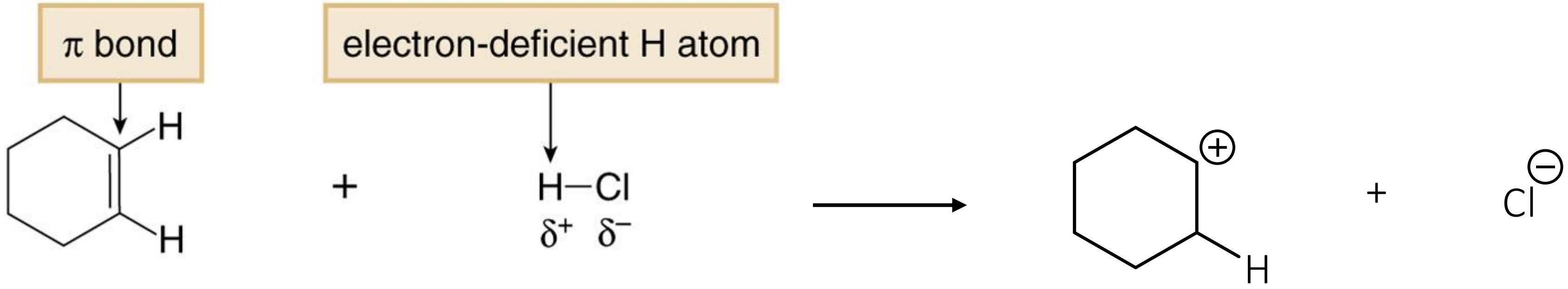


$$CH_3-\overset{\overset{\large O}{\|}}{C}-H + {}^{\ominus}OH \longrightarrow CH_3-\underset{\underset{\large OH}{|}}{\overset{\overset{\large O^{\ominus}}{|}}{C}}-H$$

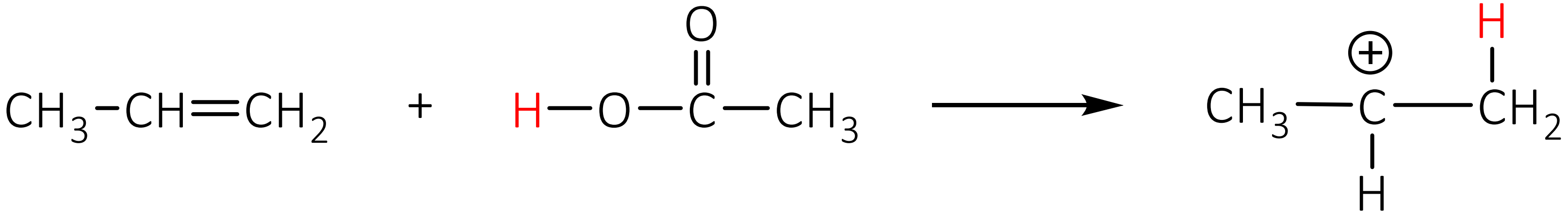
Example 2B |



Example 3A |

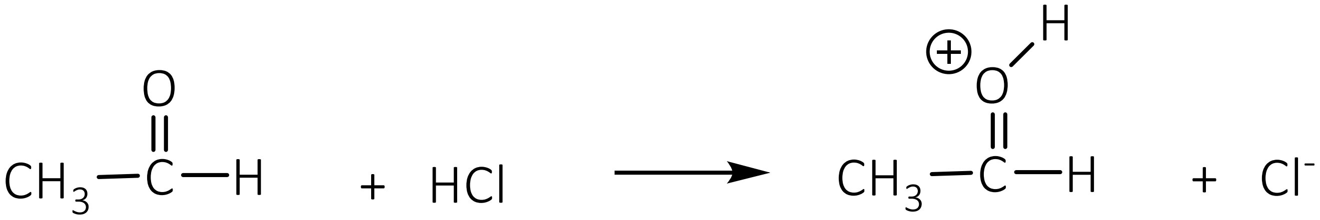


Example 3B |



$$CH_3-CH=CH_2 + H-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\oplus}{C}}-\overset{\overset{H}{|}}{CH_2}$$

Example 3C |



$$CH_3-\overset{\overset{O}{\|}}{C}-H \;+\; HCl \longrightarrow CH_3-\overset{\overset{\overset{\oplus}{O}-H}{\|}}{C}-H \;+\; Cl^-$$

acetaldehyde

References

1) Smith, J. (2010). *Organic Chemistry*: McGraw-Hill Education.
2) Solomons, T. W. G.; Fryhle, C. *Organic Chemistry; John Wiley & Sons, 2009.*
3) Wade, L. G. *Organic Chemistry; Pearson Prentice Hall, 2010.*
4) Pine, S. H.; Hendrickson, J. B. *Organic chemistry; McGraw-Hill, 1980.*
5) สุนันทา วิบูลย์จันทร์ *เคมีอินทรีย์*. สำนักพิมพ์เอ็นดับเบิลมีเดีย จำกัด, 2548.
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