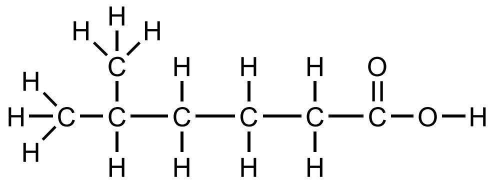
CHM 3140 Organic Chemistry I, Dr. Laurie S. Starkey, Cal Poly Pomona

Chapter 2 (Klein) - Drawing Organic Molecules & Resonance

Condensed formulas (Klein 2.1) to represent organic molecules



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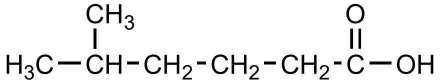
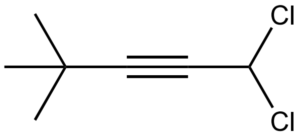


$H_3C-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

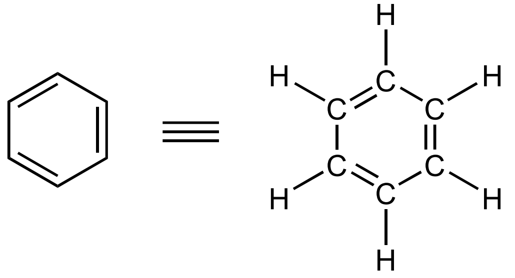
= $(CH_3)_2CH(CH_2)_3CO_2H$

Line drawings (Klein 2.2) are a short-hand way to draw carbon structures

- end points and intersections represent C atoms
- omit H's attached to C's



A



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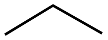
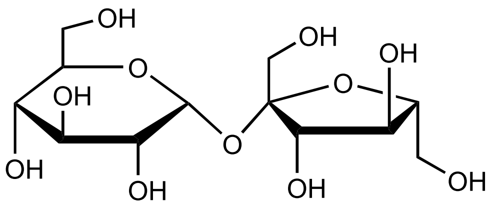


≡ CH CH CH

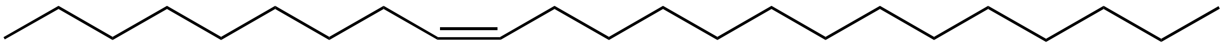
C



number of carbon atoms?

number of carbon atoms?

D



which is which?

one makes life sweet

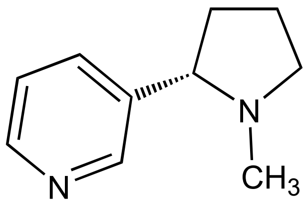
one is a housefly sex pheromone

one is for grilling burgers

one is a carcinogen

Shown below is the structures of nicotine, a stimulant in e-cigarettes that is as addictive as heroin.

- **Draw in any missing hydrogen atoms.**
- **What is the molecular formula of nicotine?** Use format $C_xH_yN_z$.



nicotine formula:______________

Try SkillBuilders 2.1, 2.2

Draw expanded structures (draw all atoms), given the following condensed formulas.

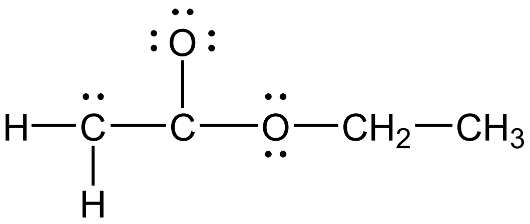
$(CH_3CH_2)_2CHCO_2CH_2CH_3$

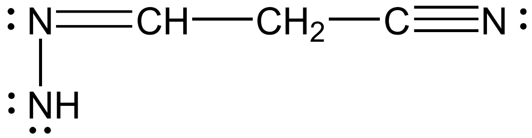
$NH_2CH_2CHBrC(CH_3)_2CH{=}C(CH_2OH)_2$

Provide bond-line drawings for each of the compounds above.

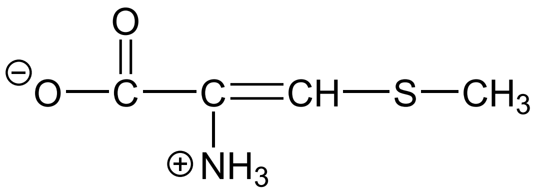
Identifying lone pairs and formal charges on given drawings. (Klein 2.3, 2.4)

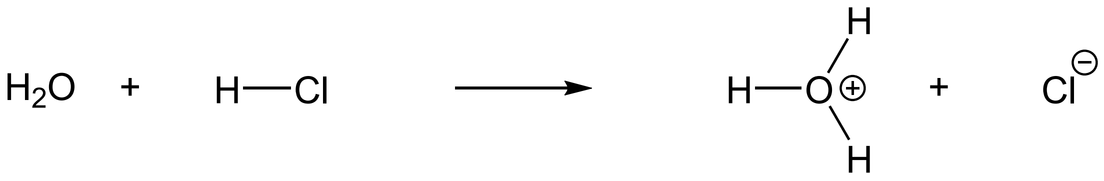
Identify missing **formal charges** on the following structures (all lone pairs are shown).





Identify missing **lone pairs** on the following structures (all formal charges are shown).





After completing all of the above Lewis structures,
circle any atoms that are missing an octet.

Try SkillBuilders 2.3, 2.4

Draw the Lewis structure of nitric acid, HNO_3

Understanding Resonance (Klein 2.7 – 2.12)

1. Any compound for which more than one Lewis structure may be written is not accurately described by any single structure. **The actual structure is a resonance hybrid of all possible Lewis structures** (NOT "flipping back and forth" between resonance forms). The various structures are called *contributing structures* or *resonance structures* or *resonance forms*.

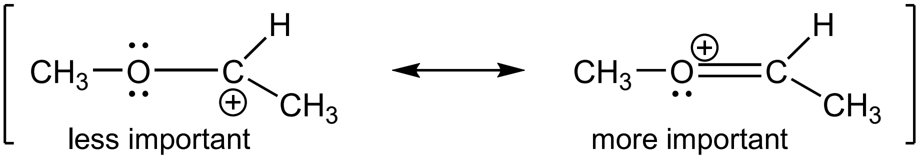
2. **The resonance hybrid is more stable than any of the contributing resonance structures.**
   - The hybrid is therefore said to be *stabilized by resonance* or *resonance stabilized* (by an amount of energy called the "resonance energy").

3. **Resonance is the interaction of electrons in *p* orbitals (described as delocalization of e^-).**
   - Only π and nonbonded electron density is reorganized in resonance (no σ bonds break).
   - *No atoms move* (no change in bond length, bond angles).
   - Since electrons are not being added or removed, there is *no change in overall charge*.

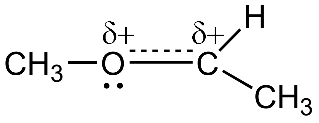
Rules for Estimating Relative Importance of Resonance Structures

The resonance hybrid most closely resembles the resonance form(s) that contributes most to the hybrid. The better the Lewis structure of a given resonance form, the greater its contribution.

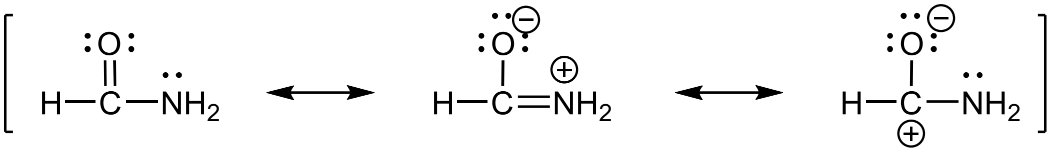
1. The greater the number of **filled octets**, the better the Lewis structure. You might notice that a structure with more covalent bonds is better, since more atoms will have complete octets.



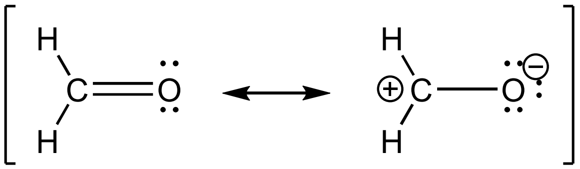
resonance hybrid:
(actual structure)

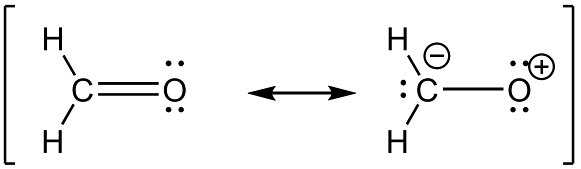


2. The structure with **fewer formal charges** is the best Lewis structure. If the species already has a net charge, creation of new charges is not favorable. For such charged compounds, the goal in drawing resonance forms is to *delocalize the charge* – relocate it to as many different positions as possible.

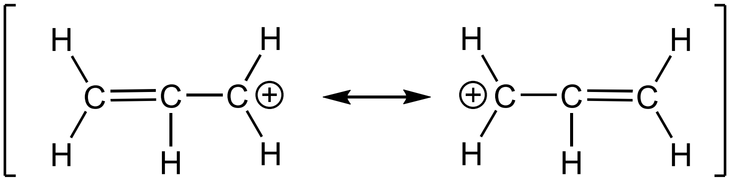


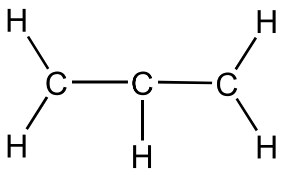
3. Other things being equal, a structure with a **negative charge on the more electronegative element** is a better Lewis structure. Similarly, a positive charge on a less electronegative element is a better Lewis structure.


important resonance


not important resonance (unlikely)

4. Resonance forms that are **equivalent** have no difference in stability and contribute equally.

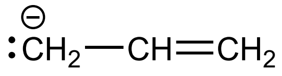

"allyl" carbocation (both forms are equally important)


resonance hybrid

Try SkillBuilders 2.5, 2.6

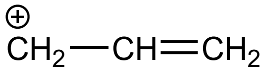
Looking for Resonance/Delocalization of Electrons (3 main types/patterns*) (Klein 2.10)

1. lone pair next to a pi bond ("**allylic" lone pair**)



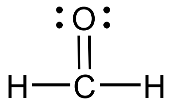
$:\overset{\ominus}{C}H_2-CH=CH_2$

2. vacancy (missing octet) next to a pi bond (**allylic carbocation**)



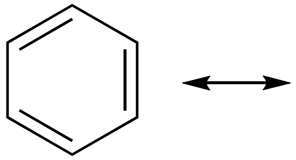
$\overset{\oplus}{C}H_2-CH=CH_2$

3. pi bond between two different elements (**carbonyl-like** resonance)
   electrons move toward the more electronegative element



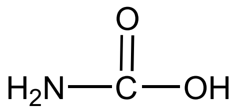
$H-\overset{\overset{:\ddot{O}:}{\|}}{C}-H$

Note: we will encounter a fourth important type of resonance later, called **aromatic resonance, that is found in molecules like benzene*



benzene

Draw and rank all possible resonance forms (explain rankings)



$H_2N-\overset{\overset{O}{\|}}{C}-OH$

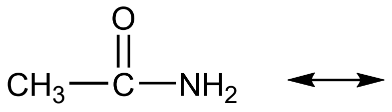
Try SkillBuilders 2.7, 2.8 and
Conceptual Checkpoints 2.18–2.25

Hybridization and Resonance: Localized and Delocalized Lone Pairs (Klein 2.13)

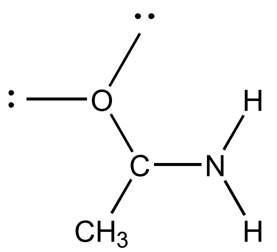
A lone pair that is involved in resonance is described as being ________________________ because it is spread out over multiple atoms.

A ___________________ lone pair is at a single location (not involved in resonance).

What is the hybridization of the nitrogen atom shown below?

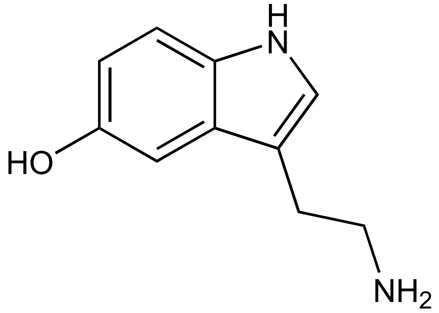


$CH_3-\overset{\overset{O}{||}}{C}-NH_2 \longleftrightarrow$



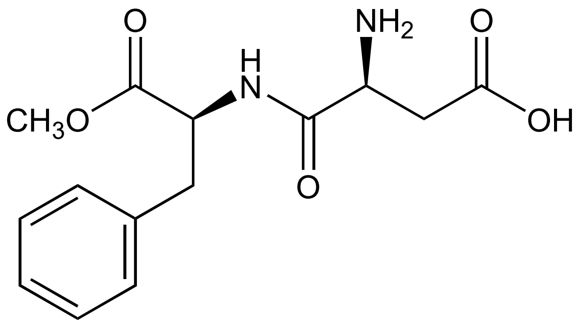
An "**allylic**" **lone pair** must be in a *p* orbital in order to have resonance delocalization! Resonance never moves atoms, so hybridization is *sp*^{2} throughout all resonance forms.

Add all missing lone pairs, and identify each as *localized (L)* or *delocalized (D).*



Serotonin

A neurotransmitter tied to positive mood (impacted by antidepressant medications, and psychedelic mushrooms). Plays a role in sleep, appetite and memory.



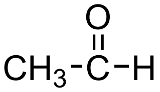
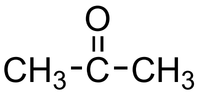
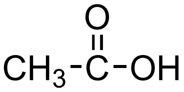
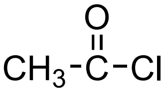
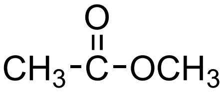
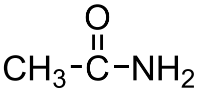
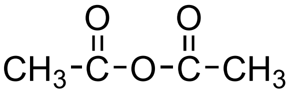
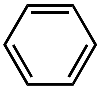
Aspartame

A ~zero-calorie artificial sweetener that is 200 times sweeter than sucrose (table sugar)

Try SkillBuilder 2.9

Functional Groups (Klein 2.3) Various arrangements of elements have predictable behavior. We will learn about the following "functional groups" throughout the year of Organic Chemistry.

Note: "R" represents any carbon group.

	Functional Group	Example	Abbreviation	Name
CHM 3140	alkane	CH_4	RH	methane
	alkyl halide	CH_3Cl	RX or RCl	chloromethane (methyl chloride)
	alkene	$H_2C=CH_2$	R_2CCR_2	ethene (ethylene)
	alkyne	$HC\equiv CH$	RCCR	ethyne (acetylene)
CHM 3150	alcohol	CH_3OH	ROH	methanol (methyl alcohol)
	ether	CH_3OCH_3	ROR or R_2O	methoxymethane (dimethyl ether)
	amine	CH_3NH_2	R_3N	methanamine (methyl amine)
	aldehyde	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}H$	RCHO	ethanal (acetaldehyde)
	ketone	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}CH_3$	RCOR or R_2CO	2-propanone (acetone)
	carboxylic acid	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}OH$	RCO_2H	ethanoic acid (acetic acid)
	acid chloride (acyl halide)	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}Cl$	RCOCl	ethanoyl chloride (acetyl chloride)
	ester	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}OCH_3$	RCO_2R	methyl ethanoate (methyl acetate)
	amide	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}NH_2$	$RCONR_2$	ethanamide (acetamide)
	anhydride	 $CH_3\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}O\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}CH_3$	RCO_2COR or $(RCO)_2O$	ethanoic anhydride (acetic anhydride)
	nitrile	CH_3CN	RCN	ethanenitrile (acetonitrile)
	aromatic		ArH	benzene

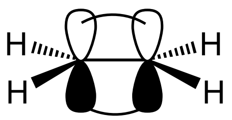
Chapter 2 Summary (Klein textbook) - Molecular Representations & Resonance

(Klein section numbers, **SB** = SkillBuillers, **CC** = Conceptual Checkpoints)

- I. Condensed formulas, bond-line drawings (2.1, 2.2, **SB 2,1, 2.2**)
  - A) 3D bond-line structures (2.6)
- II. Identifying lone pairs and formal charges (2.4, 2.5, **SB 2.3, 2.4**)
- III. Resonance (2.7-2.12)
  - A) moves π and nonbonded electrons in *p* orbitals to stabilize a molecule (2.7, 2.9, **SB 2.6**)
  - B) curved arrows show the redistribution of electron density (2.8, **SB 2.5**)
  - C) resonance forms can be ranked (find most important contributor, etc.) (2.11, **SB 2.7**)
  - D) drawing a resonance hybrid (2.12, **SB 2.8**)
  - E) identifying localized and delocalized lone pairs (2.13, **SB 2.9**)
    - a. sp^2 hybridization for atoms involved in resonance
  - F) three general types (*i.e.*, things to look for) (2.10, **CC** 2.18-2.25):
    - a. lone pair next to a π bond ("allylic" lone pair)
    - b. vacancy next to a π bond (allylic carbocation/empty *p* orbital)
    - c. bond between two different atoms (carbonyl-like)
- IV. Introduction to Functional Groups (FG) (2.3)

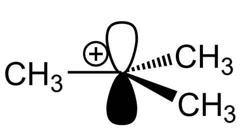
A *p* orbital can be part of a pi bond, can contain an allylic lone pair, or can be empty.

$H_2\mathbf{C}{=}CH_2$

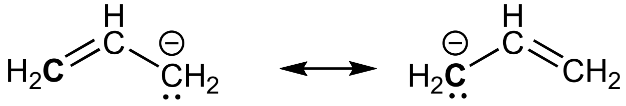


This sp^2-hybridized **C** forms a π bond with an adjacent *p* orbital.

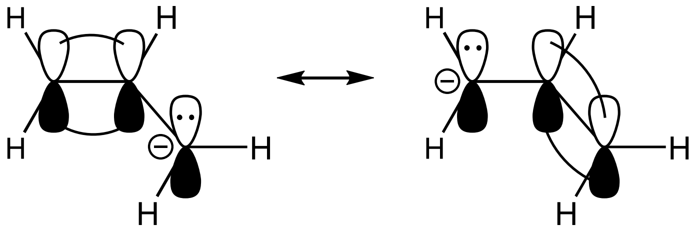
$\overset{\oplus}{\mathbf{C}}(CH_3)_3$



This sp^2-hybridized **C** has an empty *p* orbital (carbocation).



All three carbon atoms are sp^2-hybridized.



This sp^2-hybridized **C** is involved in resonance. It contains a partial π bond and δ- charge.

The resonance hybrid: