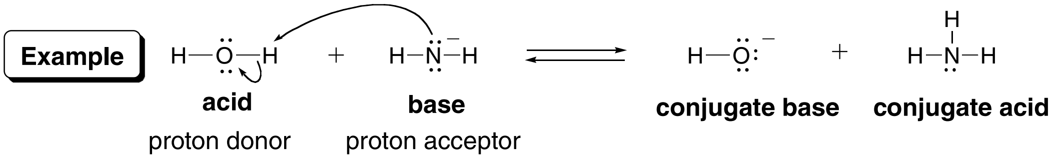
Chapter 2: Acids and Bases

◆ A comparison of Brønsted–Lowry and Lewis acids and bases

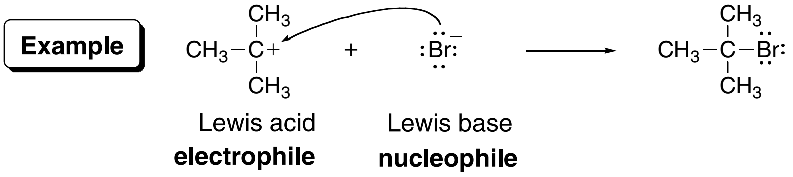
Type	Definition	Structural feature	Examples
Brønsted–Lowry acid (2.1)	proton donor	a proton	HCl, H_2SO_4, H_2O, CH_3COOH, TsOH
Brønsted–Lowry base (2.1)	proton acceptor	a lone pair *or* a π bond	^{-}OH, $^{-}OCH_3$, H^{-}, $^{-}NH_2$, $CH_2{=}CH_2$
Lewis acid (2.8)	electron pair acceptor	a proton, *or* an unfilled valence shell, *or* a partial (+) charge	BF_3, $AlCl_3$, HCl, CH_3COOH, H_2O
Lewis base (2.8)	electron pair donor	a lone pair *or* a π bond	^{-}OH, $^{-}OCH_3$, H^{-}, $^{-}NH_2$, $CH_2{=}CH_2$

◆ Acid–base reactions

[1] A Brønsted–Lowry acid donates a proton to a Brønsted–Lowry base (2.2).



[2] A Lewis base donates an electron pair to a Lewis acid (2.8).



- Electron-rich species react with electron-poor ones.
- Nucleophiles react with electrophiles.

◆ Important facts

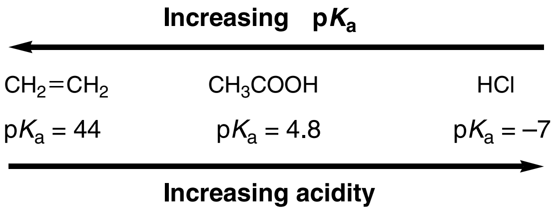
- Definition: **pK_a = –log K_a.** The **lower the pK_a**, the **stronger** the acid (2.3).

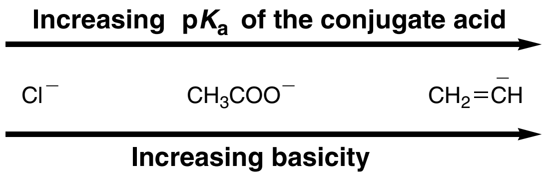
NH_3 versus H_2O

pK_a = 38 pK_a = 15.7

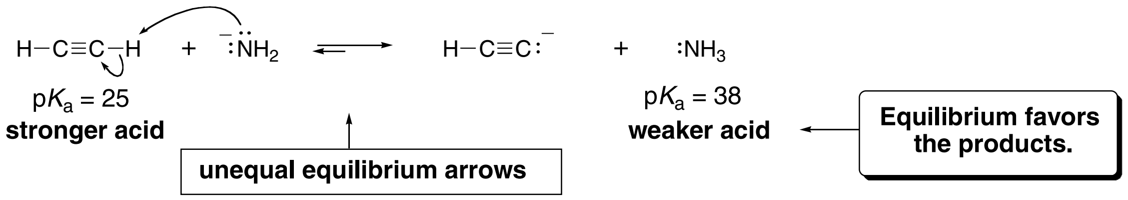
lower pK_a = stronger acid

- The stronger the acid, the weaker the conjugate base (2.3).





- In proton transfer reactions, equilibrium favors the weaker acid and weaker base (2.4).

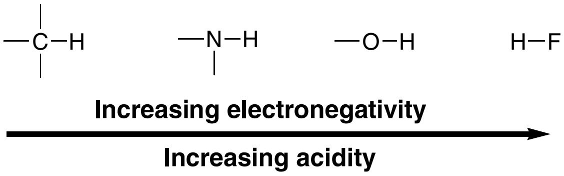


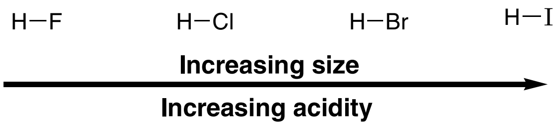
- An acid can be deprotonated by the conjugate base of any acid having a **higher pK_a** (2.4).

Acid	pK_a	Conjugate base	
$CH_3COO–H$	4.8	CH_3COO^-	
$CH_3CH_2O–H$	16	$CH_3CH_2O^-$	These bases
$HC≡CH$	25	$HC≡C^-$	can deprotonate
$H–H$	35	H^-	$CH_3COO–H$.
	higher pK_a than $CH_3COO–H$		

◆ Factors that determine acidity (2.5)

[1] **Element effects** (2.5A) The acidity of H–A increases both across a row and down a column of the periodic table.





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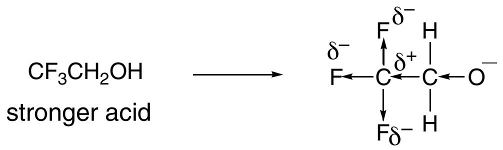
[2] **Inductive effects** (2.5B)

The acidity of H–A increases with the presence of electron-withdrawing groups in A.

$CH_3CH_2OH \longrightarrow CH_3CH_2O^-$

weaker acid

No additional electronegative atoms stabilize the conjugate base.



CF_3 withdraws electron density, stabilizing the conjugate base.

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[3] **Resonance effects** (2.5C)

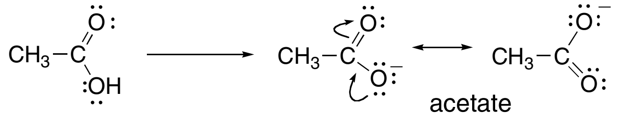
The acidity of H–A increases when the conjugate base A:⁻ is resonance stabilized.

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

ethanol

ethoxide
conjugate base

only **one** Lewis structure



acetic acid
more acidic

acetate
conjugate base

two resonance structures

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[4] **Hybridization effects** (2.5D)

The acidity of H–A increases as the percent *s*-character of the A:⁻ increases.

CH_3CH_3	$CH_2{=}CH_2$	$H-C{\equiv}C-H$
ethane	ethylene	acetylene
pK_a = 50	pK_a = 44	pK_a = 25

$\longrightarrow$

Increasing acidity

Chapter 2: Answers to Problems

2.1 Brønsted–Lowry acids are **proton donors** and must contain a hydrogen atom.
Brønsted–Lowry bases are **proton acceptors** and must have an available electron pair (either a lone pair or a π bond).

a. $H\ddot{\underset{..}{Br}}:$ **acid** $\ddot{N}H_3$ **acid** CCl_4 not an acid—no H

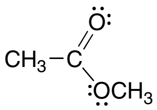
b. CH_3CH_3 no lone pairs or π bonds not a base

$(CH_3)_3C\ddot{\underset{..}{O}}:^-$ lone pairs on O **base**

$H-C\equiv C-H$ **base**—π bonds

c. $CH_3CH_2\ddot{\underset{..}{O}}H$ **base**—lone pairs on O **acid**—contains H atoms

$CH_3CH_2CH_2CH_3$ not a base—no lone pairs or π bonds **acid**—contains H atoms



base—lone pairs on O's, π bond **acid**—contains H atoms

2.2 A Brønsted–Lowry base accepts a proton to form the conjugate acid. A Brønsted–Lowry acid loses a proton to form the conjugate base.

a. $NH_3 \longrightarrow NH_4^+$

$Cl^- \longrightarrow HCl$

$(CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}\overset{+}{\underset{..}{O}}H$

b. $HBr \longrightarrow Br^-$

$HSO_4^- \longrightarrow SO_4^{2-}$

$CH_3OH \longrightarrow CH_3O^-$

2.3 Use the definitions from Answer 2.2.

$CH_2{=}CH_2 \longrightarrow \overset{+}{C}H_2{-}CH_3$

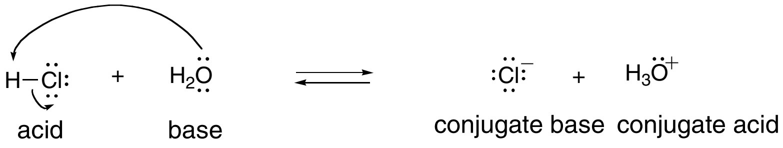
ethylene accepts a proton conjugate acid

$CH_2{=}CH_2 \longrightarrow CH_2{=}\overset{-}{\ddot{C}}H$

loses a proton conjugate base

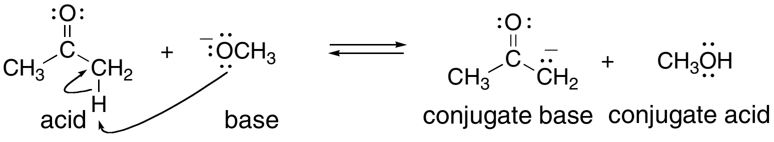
2.4 The Brønsted–Lowry base accepts a proton to form the conjugate acid. The Brønsted–Lowry acid loses a proton to form the conjugate base. Use curved arrows to show the movement of electrons (***NOT protons***). Re-draw the starting materials if necessary to clarify the electron movement.

a.



acid base conjugate base conjugate acid

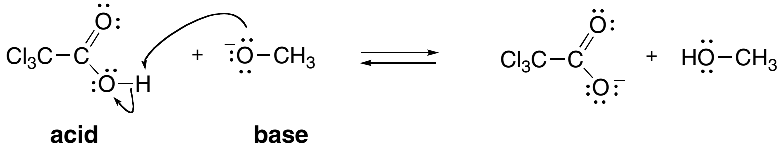
b.



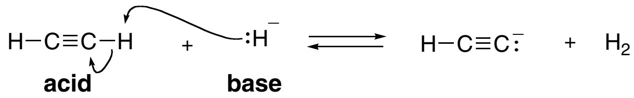
acid base conjugate base conjugate acid

2.5 To draw the products:

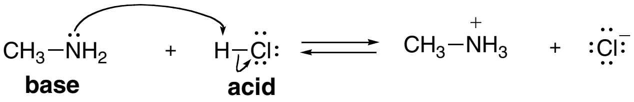
[1] Find the acid and base.
[2] Transfer a proton from the acid to the base.
[3] Check that the charges on each side of the arrows are balanced.

a.


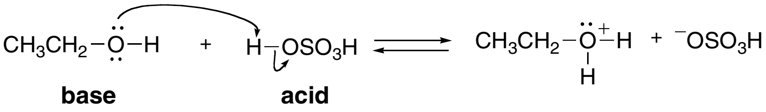
(–)1 charge on each side

b.


(–)1 charge on each side

c.


net neutral on each side

d.


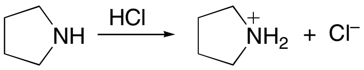
net neutral on each side

2.6 Draw the products in each reaction as in Answer 2.5.

a. $CH_3OH \xrightarrow{HCl} CH_3\overset{+}{O}H_2 + Cl^-$

b. $(CH_3CH_2)_2O \xrightarrow{HCl} (CH_3CH_2)_2\overset{+}{O}H + Cl^-$

c. $(CH_3)_3N \xrightarrow{HCl} (CH_3)_3\overset{+}{N}H + Cl^-$

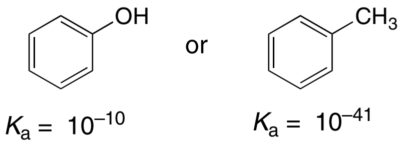
d.


2.7 The smaller the p*K*a, the stronger the acid. The larger *K*a, the stronger the acid.

a. $CH_3CH_2CH_3$ or CH_3CH_2OH

$pK_a = 50$ $\quad$ $pK_a = 16$

smaller p*K*a
stronger acid

b.


$K_a = 10^{-10}$ or $K_a = 10^{-41}$

larger *K*a
stronger acid

2.8 To convert from *K*a to p*K*a, take (–) the log of the *K*a; **p*K*a = –log *K*a**.
To convert p*K*a to *K*a, take the antilog of (–) the p*K*a.

a. $K_a = 10^{-10} \rightarrow pK_a = 10$ $\quad K_a = 10^{-21} \rightarrow pK_a = 21$ $\quad K_a = 5.2 \times 10^{-5} \rightarrow pK_a = 4.3$

b. $pK_a = 7 \rightarrow K_a = 10^{-7}$ $\quad pK_a = 11 \rightarrow K_a = 10^{-11}$ $\quad pK_a = 3.2 \rightarrow K_a = 6.3 \times 10^{-4}$

2.9 Since **strong acids form weak conjugate bases**, the basicity of conjugate bases increases with increasing pK_a of their acids. Find the pK_a of each acid from Table 2.1 and then rank the acids in order of increasing pK_a. This will also be the order of increasing basicity of their conjugate bases.

a. ← Increasing acidity

H_2O, NH_3, CH_4

pK_a = 15.7   38   50

conjugate bases: ^-OH, $^-NH_2$, $^-CH_3$

Increasing basicity →

b. ← Increasing acidity

$HC{\equiv}CH$, $CH_2{=}CH_2$, CH_4

pK_a = 25   44   50

conjugate bases: $^-C{\equiv}CH$, $^-CH{=}CH_2$, $^-CH_3$

Increasing basicity →

2.10 Use the definitions in Answer 2.9 to compare the acids. The smaller the pK_a, the larger the K_a and the stronger the acid. When a stronger acid dissolves in water, the equilibrium lies farther to the right.

HCO_2H	$(CH_3)_3CCO_2H$
formic acid	**pivalic acid**
pK_a = 3.8	pK_a = 5.0

a. smaller pK_a = larger K_a

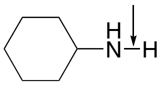
b. smaller pK_a = stronger acid

c. weaker acid = stronger conjugate base

d. stronger acid = equilibrium farther to the right

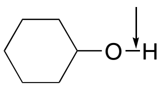
2.11 To estimate the pK_a of the indicated bond, find a similar bond in the pK_a table (H bonded to the same atom with the same hybridization).

a.



For NH_3, pK_a is 38.
estimated pK_a = 38

b.



For CH_3CH_2OH, pK_a is 16.
estimated pK_a = 16

c. $BrCH_2COO\overset{\downarrow}{-}H$

For CH_3COOH, pK_a is 4.8.
estimated pK_a = 5

2.12 Label the acid and the base and then transfer a proton from the acid to the base. To determine if the reaction will proceed as written, compare the pK_a of the acid on the left with the conjugate acid on the right. **The equilibrium always favors the formation of the weaker acid and the weaker base.**

a. $CH_2{=}CH_2 + H:^- \rightleftharpoons CH_2{=}\overset{-}{\ddot{C}}H + H_2$

$CH_2{=}CH_2$	$H:^-$	$CH_2{=}\overset{-}{\ddot{C}}H$	H_2
acid	base	conjugate base	conjugate acid
pK_a = 44			pK_a = 35
weaker acid			

Equilibrium favors the **starting materials.**

b. $CH_4 + {}^-\!:\ddot{O}H \rightleftharpoons {}^-\!:CH_3 + H_2\ddot{O}:$

CH_4	$^-:\ddot{O}H$	$^-:CH_3$	$H_2\ddot{O}:$
acid	base	conjugate base	conjugate acid
pK_a = 50			pK_a = 15.7
weaker acid			

Equilibrium favors the **starting materials.**

c. $CH_3COOH + CH_3CH_2\ddot{O}:^- \rightleftharpoons CH_3COO^- + CH_3CH_2\ddot{O}H$

CH_3COOH	$CH_3CH_2\ddot{O}:^-$	CH_3COO^-	$CH_3CH_2\ddot{O}H$
acid	base	conjugate base	conjugate acid
pK_a = 4.8			pK_a = 16
			weaker acid

Equilibrium favors the **products.**

d. $:\ddot{\underset{\cdot\cdot}{Cl}}:^- + CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}H \rightleftharpoons H\ddot{\underset{\cdot\cdot}{Cl}}: + CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}:^-$

base	acid pK_a = 16 **weaker acid**	conjugate acid pK_a = –7	conjugate base

Equilibrium favors the **starting materials.**

2.13 An acid can be deprotonated by the conjugate base of any acid with a higher pK_a.

CH_3COOH
pK_a = 4.8
Any base having a conjugate acid with a pK_a higher than 4.8 can deprotonate this acid.

Acid	**pK_a**	**Conjugate base**	
HCl	–7	Cl^-	not strong enough
HC≡CH	25	$HC{\equiv}C^-$	strong enough
H_2	35	H^-	

HC≡CH
pK_a = 25
All of these acids have a higher pK_a than HC≡CH, and a conjugate base that can deprotonate HC≡CH.

Acid	**pK_a**	**Conjugate base**
H_2	35	H^-
NH_3	38	$^-NH_2$
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

2.14 An acid can be deprotonated by the conjugate base of any acid with a higher pK_a.

CH_3CN
pK_a = 25
Any base having a conjugate acid with a pK_a higher than 25 can deprotonate this acid.

Base	**Conjugate acid**	**pK_a**	
NaH	H_2	35	Only NaH and $NaNH_2$ are strong enough to deprotonate acetonitrile.
Na_2CO_3	HCO_3^-	10.2	
NaOH	H_2O	15.7	
$NaNH_2$	NH_3	38	
$NaHCO_3$	H_2CO_3	6.4	

2.15 The acidity of H–Z **increases across a row and down a column** of the periodic table.

a. NH_3, H_2O
O is farther to the right in the periodic table.
stronger acid

b. HBr, HCl
Br is farther down the periodic table.
stronger acid

c. H_2S, HBr
Br is farther across and down the periodic table.
stronger acid

2.16 Compare the most acidic protons in each compound to determine the stronger acid.

a. $CH_3CH_2CH_2NH_2$ or $(CH_3)_3N$
N–H bond C–H bond
N is farther to the right in the periodic table.
stronger acid

b. $CH_3CH_2OCH_3$ or $CH_3CH_2CH_2OH$
C–H bond O–H bond
O is farther to the right in the periodic table.
stronger acid

2.17 Look at the element bonded to the acidic H and decide its acidity based on the periodic trends. **Farther right and down the periodic table is more acidic.**

most acidic ↓

a. $CH_3CH_2CH_2CH_2O\mathbf{H}$

Molecule contains C–H and O–H bonds.
O is farther right; therefore,
O–H hydrogen is the most acidic.

most acidic ↓

b. $\mathbf{H}OCH_2CH_2CH_2NH_2$

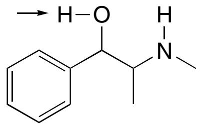
Molecule contains C–H, N–H, and O–H bonds.
O is farthest right; therefore,
O–H hydrogen is the most acidic.

most acidic ↓

c. $(CH_3)_2NCH_2CH_2CH_2N\mathbf{H}_2$

Molecule contains C–H and N–H bonds.
N is farther right; therefore,
N–H hydrogen is the most acidic.

2.18 The acidity of HA increases across the periodic table. Pseudoephedrine contains C–H, N–H, and O–H bonds. The O–H bond is most acidic.



pseudoephedrine

2.19 **More electronegative atoms stabilize the conjugate base, making the acid stronger.** Compare the electron-withdrawing groups on the acids below to decide which is a stronger acid **(more electronegative groups = more acidic).**

a. $ClCH_2COOH$ or FCH_2COOH more acidic

F is more electronegative than Cl, making the O–H bond in the acid on the right **more acidic.**

b. Cl_2CHCH_2OH or $Cl_2CHCH_2CH_2OH$

Cl is closer to the acidic O–H bond. **more acidic**

Cl is farther from the O–H bond.

c. CH_3COOH or O_2NCH_2COOH more acidic

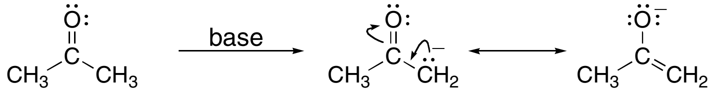
NO_2 is electron withdrawing, making the O–H bond in the acid on the right **more acidic.**

2.20 **More electronegative groups stabilize the conjugate base, making the acid stronger.**

↓
$HOCH_2CO_2H$
an α-hydroxy acid
The extra OH group contains an electronegative O, which stabilizes the conjugate base.
stronger acid

CH_3CO_2H
acetic acid

2.21 The acidity of an acid increases when the conjugate base is resonance stabilized. Compare the conjugate bases of acetone and propane to explain why acetone is more acidic.



acetone
pK_a = 19.2

2 resonance structures
more stable conjugate base
Acetone is more acidic.

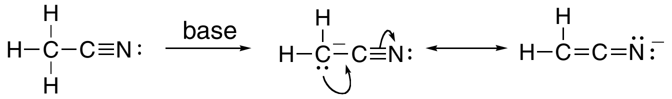
One resonance structure places the (–) charge on the more electronegative O atom. This is especially good.

$CH_3CH_2CH_3 \xrightarrow{\text{base}} CH_3CH_2\ddot{C}H_2^-$

propane
pK_a = 50

only one Lewis structure
less stable conjugate base
(Any C–H bond in the starting material can be removed.)

2.22 The acidity of an acid increases when the conjugate base is resonance stabilized. Acetonitrile has a resonance-stabilized conjugate base, which accounts for its acidity.



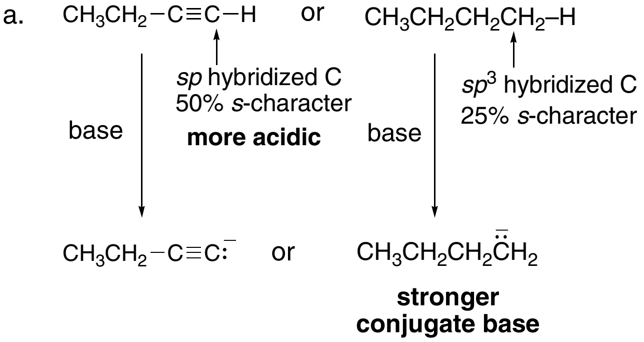
$H_3C{-}C{\equiv}N: \xrightarrow{\text{base}} H_2\ddot{C}^-{-}C{\equiv}N: \longleftrightarrow H_2C{=}C{=}\ddot{N}:^-$

acetonitrile
(one Lewis structure)

The negative charge is stabilized by delocalization on the C and N atoms.

Having the (–) charge on the electronegative N atom adds stability.

2.23 **Increasing percent *s*-character makes an acid more acidic.** Compare the percent *s*-character of the carbon atoms in each of the C–H bonds in question. A stronger acid has a weaker conjugate base.

a. 

$CH_3CH_2{-}C{\equiv}C{-}H$ or $CH_3CH_2CH_2CH_2{-}H$

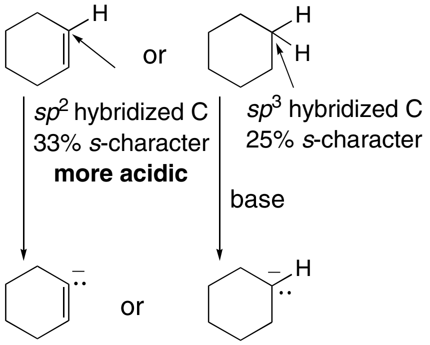
sp hybridized C
50% *s*-character
more acidic

sp^3 hybridized C
25% *s*-character

base

$CH_3CH_2{-}C{\equiv}C:^-$ or $CH_3CH_2CH_2\ddot{C}H_2^-$

stronger conjugate base

b. 

sp^2 hybridized C
33% *s*-character
more acidic

sp^3 hybridized C
25% *s*-character

base

stronger conjugate base

2.24 To compare the acids, first **look for element effects**. Then identify electron-withdrawing groups, resonance, or hybridization differences.

a. $CH_3CH_2CH_3$ — C is farthest left in the periodic table. **CH bond is least acidic.**

$CH_3CH_2NH_2$ — **intermediate acidity**

CH_3CH_2OH — O is farthest right in the periodic table. **OH bond is most acidic.**

b. $CH_3CH_2CH_2OH$ — OH group **least acidic**

CH_3CH_2COOH — **intermediate acidity**

$BrCH_2COOH$ — Br is electron withdrawing and the conjugate base is resonance stabilized. **most acidic**

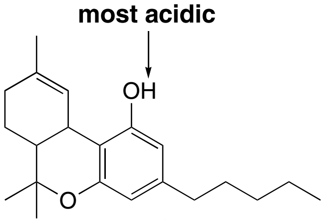
c. $(CH_3)_3N$ — C is farthest left in the periodic table. **CH bond is least acidic.**

$CH_3CH_2NH_2$ — **intermediate acidity**

CH_3CH_2OH — O is farthest right in the periodic table. **OH bond is most acidic.**

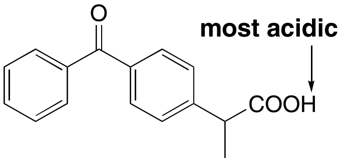
2.25 Look at the element bonded to the acidic H and decide its acidity based on the periodic trends. **Farther right and down the periodic table is more acidic.**

a.



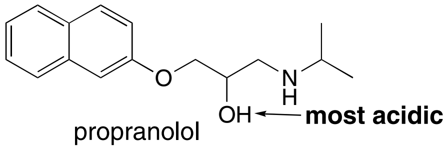
THC
tetrahydrocannabinol
The molecule contains C–H and O–H bonds.
O is farther right; therefore, O–H hydrogen is the most acidic.

b.



ketoprofen
The molecule contains C–H and O–H bonds.
O is farther right; therefore, O–H hydrogen is the most acidic.

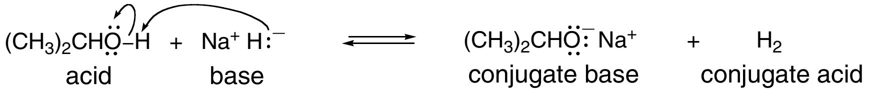
c.



propranolol
The molecule contains C–H, N–H, and O–H bonds.
O is farthest right; therefore, O–H hydrogen is the most acidic.

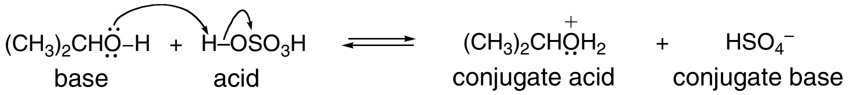
2.26 Draw the products of proton transfer from the acid to the base.

a.



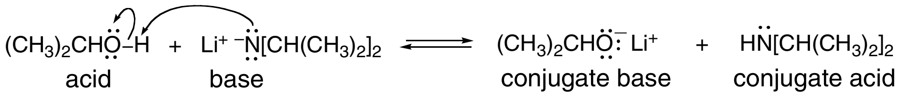
$\underset{\text{acid}}{(CH_3)_2CH\ddot{\underset{..}{O}}-H} + \underset{\text{base}}{Na^+\ H:^-} \rightleftharpoons \underset{\text{conjugate base}}{(CH_3)_2CH\ddot{\underset{..}{O}}:^-\ Na^+} + \underset{\text{conjugate acid}}{H_2}$

b.



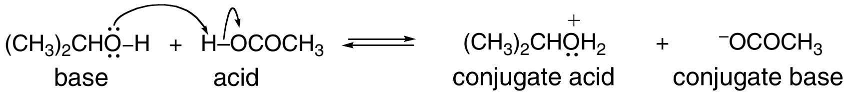
$\underset{\text{base}}{(CH_3)_2CH\ddot{\underset{..}{O}}-H} + \underset{\text{acid}}{H-OSO_3H} \rightleftharpoons \underset{\text{conjugate acid}}{(CH_3)_2CH\overset{+}{\underset{..}{O}}H_2} + \underset{\text{conjugate base}}{HSO_4^-}$

c.



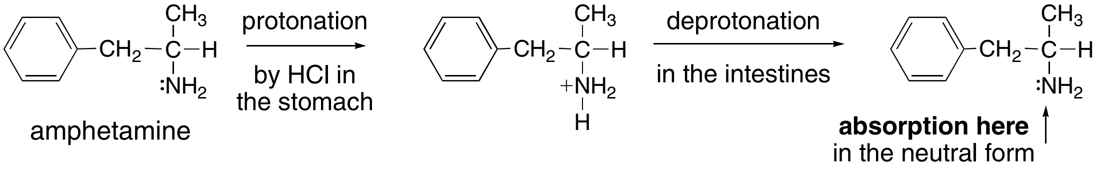
$\underset{\text{acid}}{(CH_3)_2CH\ddot{\underset{..}{O}}-H} + \underset{\text{base}}{Li^+\ {}^-\ddot{\underset{..}{N}}[CH(CH_3)_2]_2} \rightleftharpoons \underset{\text{conjugate base}}{(CH_3)_2CH\ddot{\underset{..}{O}}:^-\ Li^+} + \underset{\text{conjugate acid}}{H\ddot{N}[CH(CH_3)_2]_2}$

d.



$\underset{\text{base}}{(CH_3)_2CH\ddot{\underset{..}{O}}-H} + \underset{\text{acid}}{H-OCOCH_3} \rightleftharpoons \underset{\text{conjugate acid}}{(CH_3)_2CH\overset{+}{\underset{..}{O}}H_2} + \underset{\text{conjugate base}}{{}^-OCOCH_3}$

2.27 To cross a cell membrane, amphetamine must be in its neutral (not ionic) form.



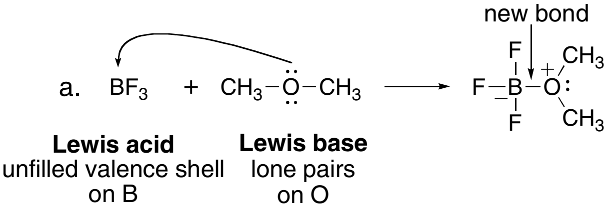
2.28 **Lewis bases are electron pair donors:** they contain a lone pair or a π bond.

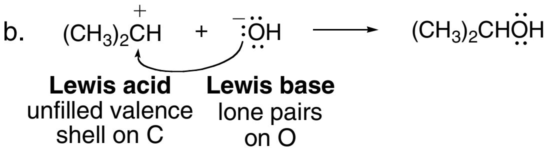
a. $\ddot{N}H_3$	b. $CH_3CH_2CH_3$	c. $H:^-$	d. $H-C\equiv C-H$
yes - has lone pair	**no** - no lone pair or π bond	**yes** - has lone pair	**yes** - has 2 π bonds

2.29 **Lewis acids are electron pair acceptors.** Most Lewis acids contain a proton or an unfilled valence shell of electrons.

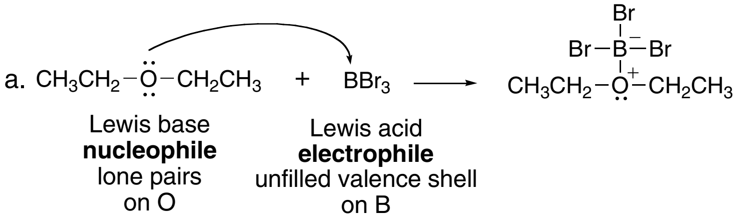
a. BBr_3	b. CH_3CH_2OH	c. $(CH_3)_3C^+$	d. Br^-
yes unfilled valence shell on B	**yes** contains a proton	**yes** unfilled valence shell on C	**no** no proton no unfilled valence shell

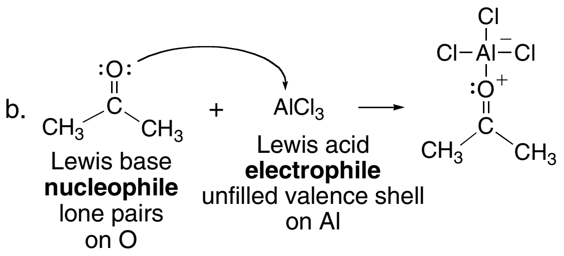
2.30 Label the Lewis acid and Lewis base and then draw the curved arrows.



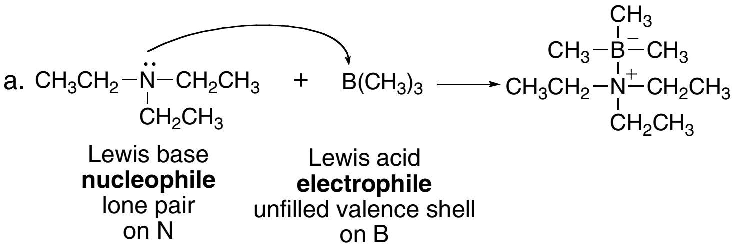


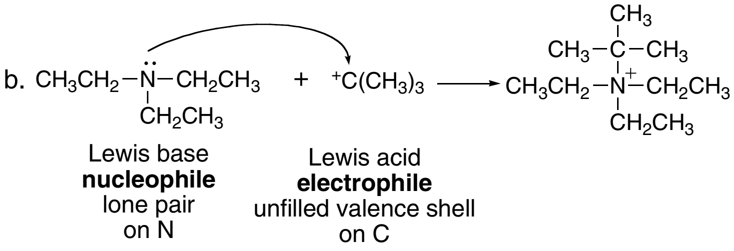
2.31 A Lewis acid is also called an **electrophile**. When a Lewis base reacts with an electrophile other than a proton, it is called a **nucleophile**. Label the electrophile and nucleophile in the starting materials and then draw the products.

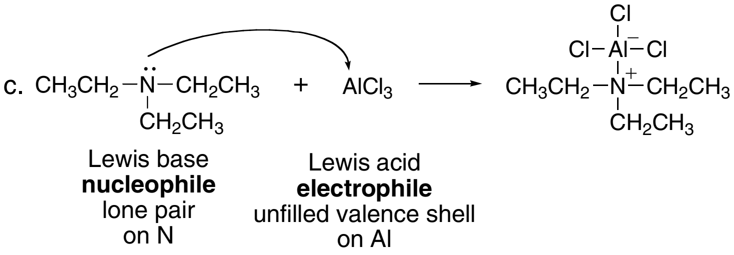




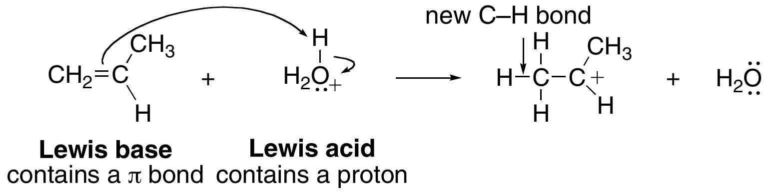
2.32 Draw the product of each reaction by using an electron pair of the Lewis base to form a new bond to the Lewis acid.







2.33 Curved arrows begin at the Lewis base and point towards the Lewis acid.



2.34 To draw the conjugate acid of a Brønsted–Lowry base, **add a proton to the base**.

a. $H_2\ddot{O}: \xrightarrow{H^+} H_3\ddot{O}^+$

b. $^-:\ddot{N}H_2 \xrightarrow{H^+} \ddot{N}H_3$

c. $HCO_3^- \xrightarrow{H^+} H_2CO_3$

d. $CH_3CH_2\ddot{N}HCH_3 \xrightarrow{H^+} CH_3CH_2\overset{+}{N}H_2CH_3$

e. $CH_3\ddot{O}CH_3 \xrightarrow{H^+} CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}-CH_3$

f. $CH_3COO^- \xrightarrow{H^+} CH_3COOH$

2.35 To draw the conjugate base of a Brønsted–Lowry acid, **remove a proton from the acid.**

a. $HCN \xrightarrow{-H^+} {}^-CN$

b. $HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$

c. $(CH_3)_2\overset{+}{N}H_2 \xrightarrow{-H^+} (CH_3)_2NH$

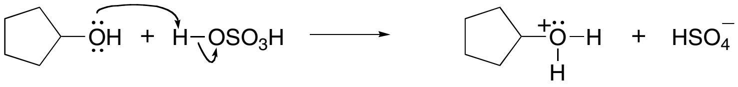
d. $HC\equiv CH \xrightarrow{-H^+} HC\equiv C^-$

e. $CH_3CH_2COOH \xrightarrow{-H^+} CH_3CH_2COO^-$

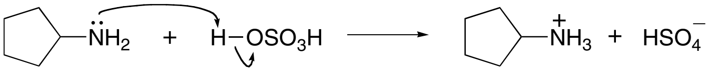
f. $CH_3SO_3H \xrightarrow{-H^+} CH_3SO_3^-$

2.36 To draw the products of an acid–base reaction, transfer a proton from the acid (H_2SO_4 in this case) to the base.

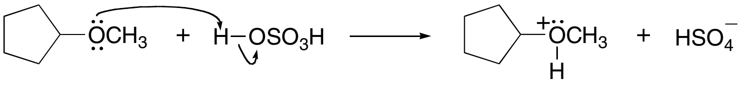
a.



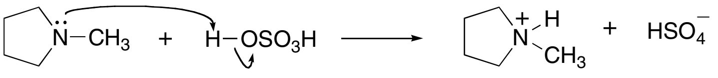
b.



c.

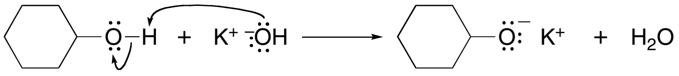


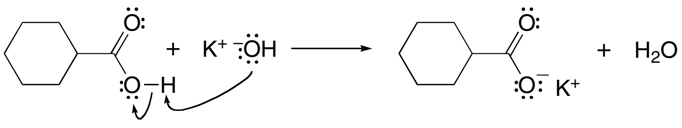
d.

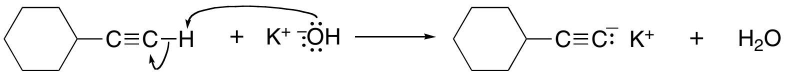


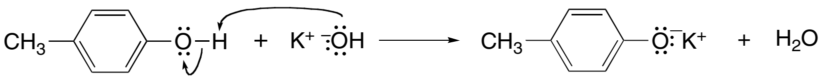
2.37 To draw the products of an acid–base reaction, transfer a proton from the acid to the base (^-OH in this case).

a.

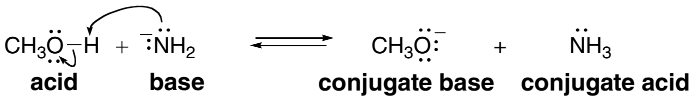


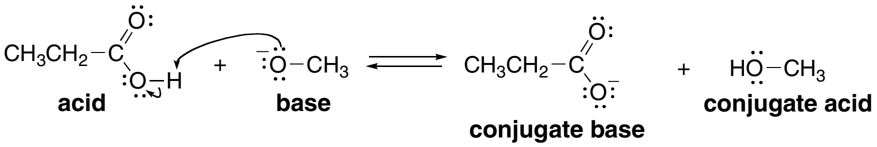
b. 

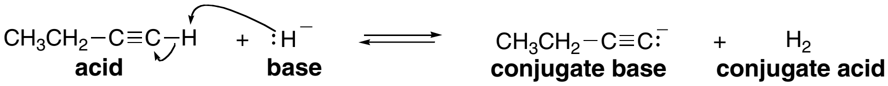
c. 

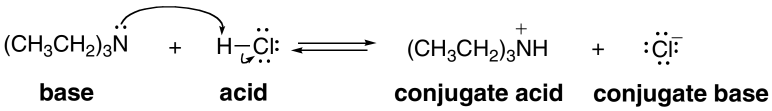
d. 

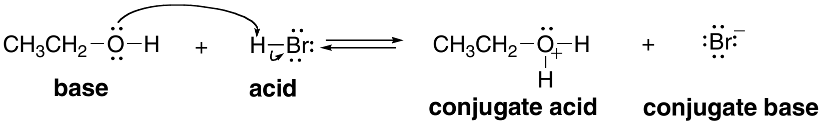
2.38 Label the Brønsted–Lowry acid and Brønsted–Lowry base in the starting materials and **transfer a proton from the acid to the base** for the products.

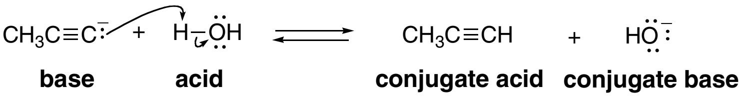
a. 

b. 

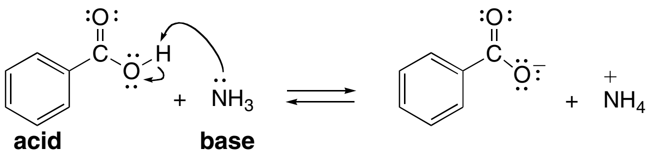
c. 

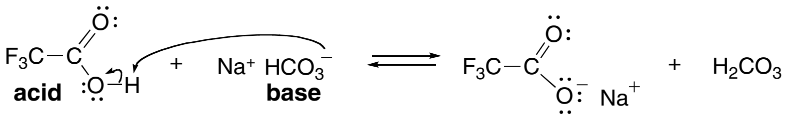
d. 

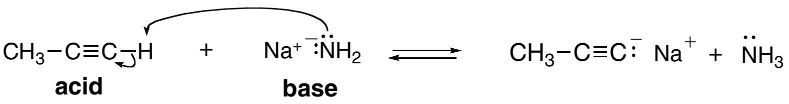
e. 

f. 

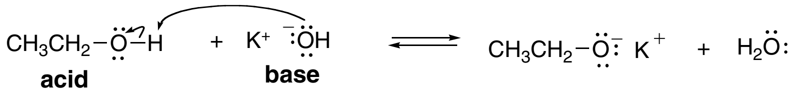
2.39 Label the acid and base in the starting materials and then draw the products of proton transfer from acid to base.

a. 

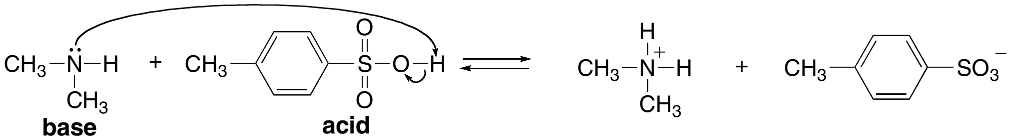
b. 

c. 

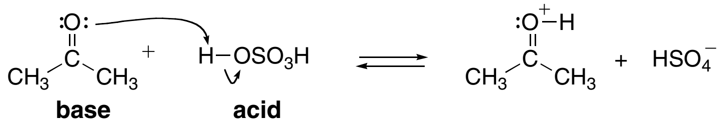
d.



e.

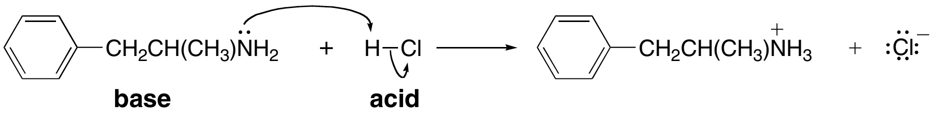


f.

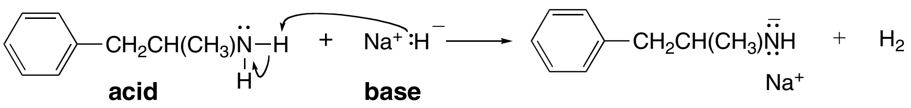


2.40 Label the acid and base in the starting materials and then draw the products of proton transfer from acid to base.

a.

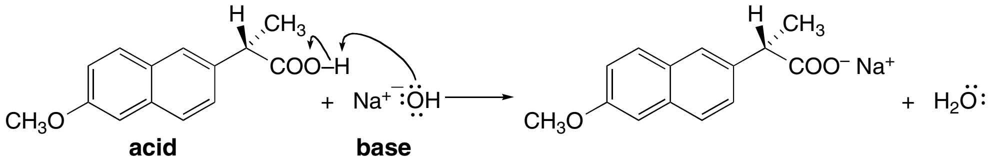


b.

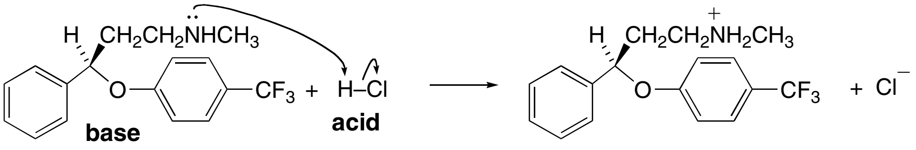


2.41 Draw the products of proton transfer from acid to base.

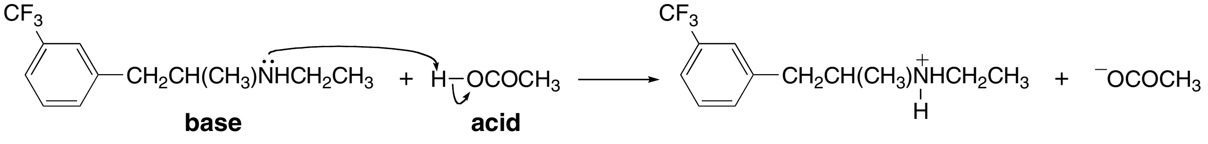
a.

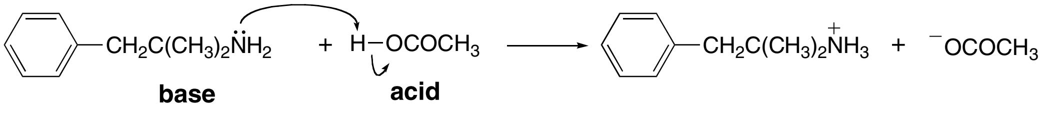


b.



2.42 Draw the products of proton transfer from acid to base.

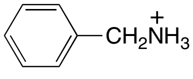




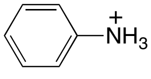
2.43 To convert p*K*a to *K*a, take the antilog of (–) the p*K*a.

a. H_2S	b. $ClCH_2COOH$	c. HCN
$pK_a = 7.0$	$pK_a = 2.8$	$pK_a = 9.1$
$K_a = 10^{-7}$	$K_a = 1.6 \times 10^{-3}$	$K_a = 7.9 \times 10^{-10}$

2.44 To convert from *K*a to p*K*a, take (–) the log of the *K*a; **p*K*a = –log *K*a**.

a. 

$K_a = 4.7 \times 10^{-10}$
$pK_a = 9.3$

b. 

$K_a = 2.3 \times 10^{-5}$
$pK_a = 4.6$

c. CF_3COOH

$K_a = 5.9 \times 10^{-1}$
$pK_a = 0.23$

2.45 An acid can be deprotonated by the conjugate base of any acid with a higher p*K*a.

a. **H_2O**
$pK_a = 15.7$
Any base with a conjugate acid having a p*K*a higher than 15.7 can deprotonate it.

Acid	pK_a	Conjugate base
CH_3CH_2OH	16	$CH_3CH_2O^-$
$HC{\equiv}CH$	25	$HC{\equiv}C^-$
H_2	35	H^-
NH_3	38	$^-NH_2$
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

Strong enough to deprotonate H_2O.

b. **NH_3**
$pK_a = 38$
Any base with a conjugate acid having a p*K*a higher than 38 can deprotonate it.

Acid	pK_a	Conjugate base
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

Strong enough to deprotonate NH_3.

c. **CH_4**
$pK_a = 50$
There is no base with a conjugate acid having a p*K*a higher than 50 in the table.

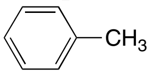
2.46 An acid can be deprotonated by the conjugate base of any acid with a higher p*K*a.

$CH_3CH_2CH_2C{\equiv}CH$
$pK_a = 25$
Any base having a conjugate acid with a p*K*a higher than 25 can deprotonate this acid.

Base	Conjugate acid	pK_a
H_2O	H_3O^+	–1.7
NaOH	H_2O	15.7
$NaNH_2$	NH_3	38
NH_3	NH_4^+	9.4
NaH	H_2	35
CH_3Li	CH_4	50

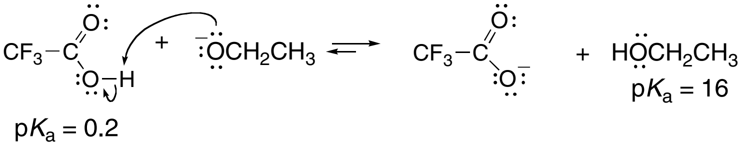
Only $NaNH_2$, NaH, and CH_3Li are strong enough to deprotonate the acid.

2.47 ^-OH can deprotonate any acid with a p*K*a < 15.7.

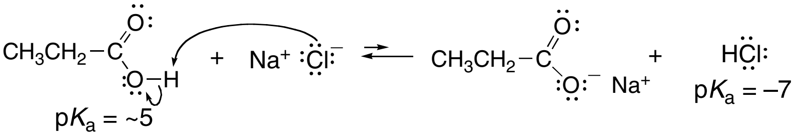
a. HCOOH	b. H_2S	c. 	d. CH_3NH_2
$pK_a = 3.8$ stronger acid deprotonated	$pK_a = 7.0$ stronger acid deprotonated	$pK_a = 41$ weaker acid	$pK_a = 40$ weaker acid

These acids are too weak to be deprotonated by ^-OH.

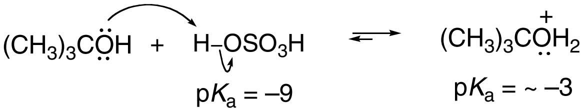
2.48 Draw the products and then compare the pK_a of the acid on the left and the conjugate acid on the right. **The equilibrium lies towards the side having the acid with a higher pK_a (weaker acid).**

a.


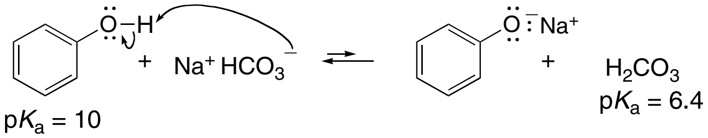
products favored

b.


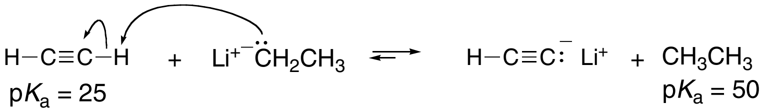
starting material favored

c.


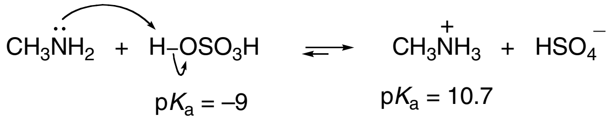
products favored

d.


starting material favored

e.


products favored

f.


products favored

2.49 Compare element effects first and then resonance, hybridization, and electron-withdrawing groups to determine the relative strengths of the acids.

a. Acidity increases across a row:
$NH_3 < H_2O < HF$

b. Acidity increases down a column:
$HF < HCl < HBr$

c. increasing acidity: $^-OH < H_2O < H_3O^+$

d. increasing acidity: $NH_3 < H_2O < H_2S$

Compare NH and OH bonds first:
acidity increases across a row.
OH is more acidic.

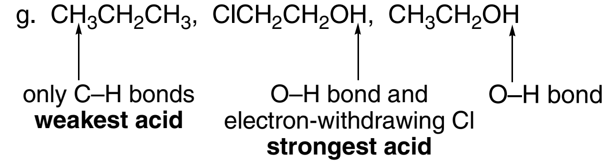
Then compare OH and SH bonds:
acidity increases down a column.
SH is more acidic.

e. Acidity increases across a row:
$CH_3CH_3 < CH_3NH_2 < CH_3OH$

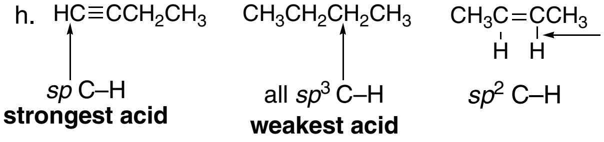
f. increasing acidity: $H_2O < H_2S < HCl$

Compare HCl and SH bonds first:
acidity increases across a row.
H–Cl is more acidic.

Compare OH and SH bonds:
acidity increases down a column.
SH is more acidic.

g.


increasing acidity: $CH_3CH_2CH_3 < CH_3CH_2OH < ClCH_2CH_2OH$

h.


increasing acidity: $CH_3CH_2CH_2CH_3 < CH_3CH{=}CHCH_3 < HC{\equiv}CCH_2CH_3$

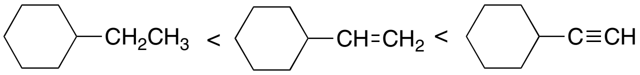
2.50 The strongest acid has the weakest conjugate base.

a. Draw the conjugate acid.
Increasing acidity of conjugate acids:
CH_3CH_3 < CH_3NH_2 < CH_3OH
increasing basicity: CH_3O^- < $CH_3\overset{-}{N}H$ < $CH_3\overset{-}{C}H_2$

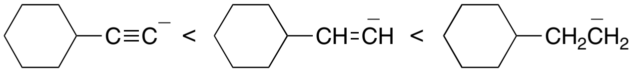
b. Draw the conjugate acid.
Increasing acidity of conjugate acids:
CH_4 < H_2O < HBr
increasing basicity: Br^- < HO^- < $^-CH_3$

c. Draw the conjugate acid.
Increasing acidity of conjugate acids:
CH_3CH_2OH < CH_3COOH < $ClCH_2COOH$
increasing basicity: $ClCH_2COO^-$ < CH_3COO^- < $CH_3CH_2O^-$

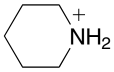
d. Draw the conjugate acid.
Increasing acidity of conjugate acids:



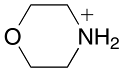
increasing basicity:



2.51 **More electronegative atoms stabilize the conjugate base by an electron-withdrawing inductive effect, making the acid stronger.** Thus, an O atom increases the acidity of an acid.



pK_a = 11.1



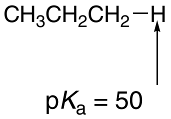
The O atom makes this cation the stronger acid.
pK_a = 8.33

2.52 In both molecules the OH proton is the most acidic H. In addition, compare the percent *s*-character of the carbon atoms in each molecule. Nearby C's with a higher percent *s*-character can help to stabilize the conjugate base.

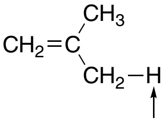
$HC{\equiv}CCO_2H$
pK_a = 1.8
The *sp* hybridized C's of the triple bond have a higher percent *s*-character than an *sp*^{3} hybridized C, so they pull electron density towards them, stabilizing the conjugate base.
stronger acid

$CH_3CH_2CO_2H$
pK_a = 4.9

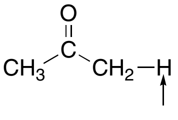
2.53



pK_a = 50



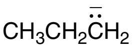
pK_a = 43



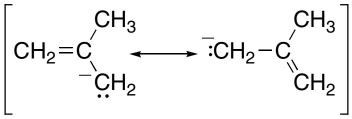
pK_a = 19.2

The negative charge on O is good. This makes this resonance structure especially good.

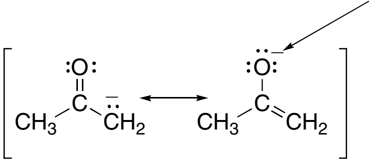
conjugate base:



one Lewis structure
weakest acid

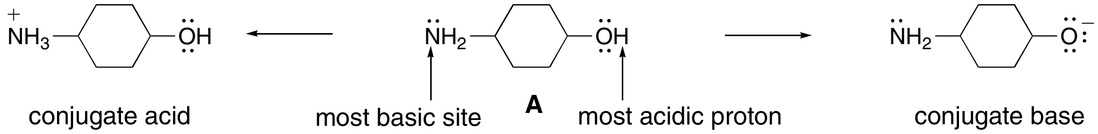


two resonance structures
negative charge delocalized
on two carbons

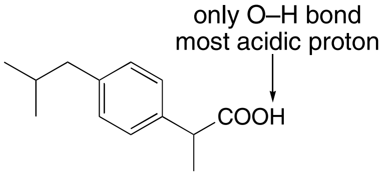


two resonance structures
negative charge delocalized
on one O and one C
strongest acid

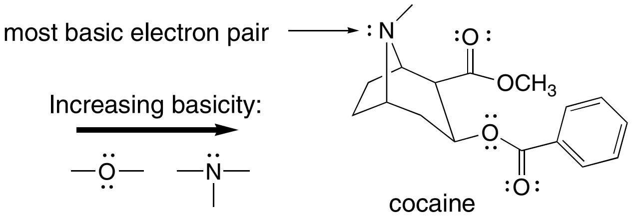
2.54 To draw the conjugate acid, look for the most basic site and protonate it. To draw the conjugate base, look for the most acidic site and remove a proton.



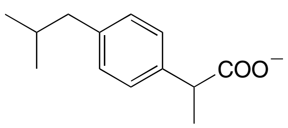
2.55 Remove the most acidic proton to form the conjugate base. Protonate the most basic electron pair to form the conjugate acid.



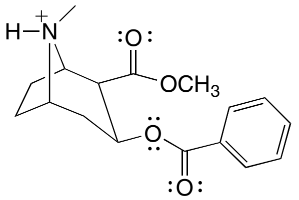
ibuprofen



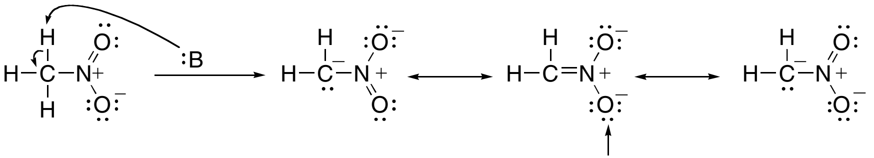
conjugate base:



conjugate acid:

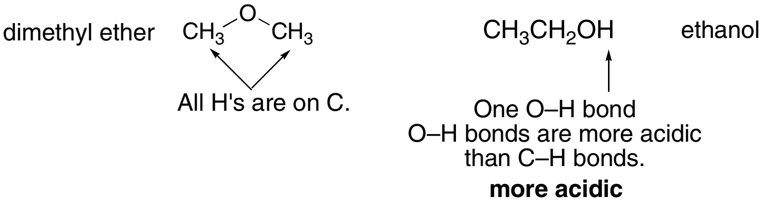


2.56 **A lower pK_a means a stronger acid.** The pK_a is low for the C–H bond in CH_3NO_2 due to resonance stabilization of the conjugate base.

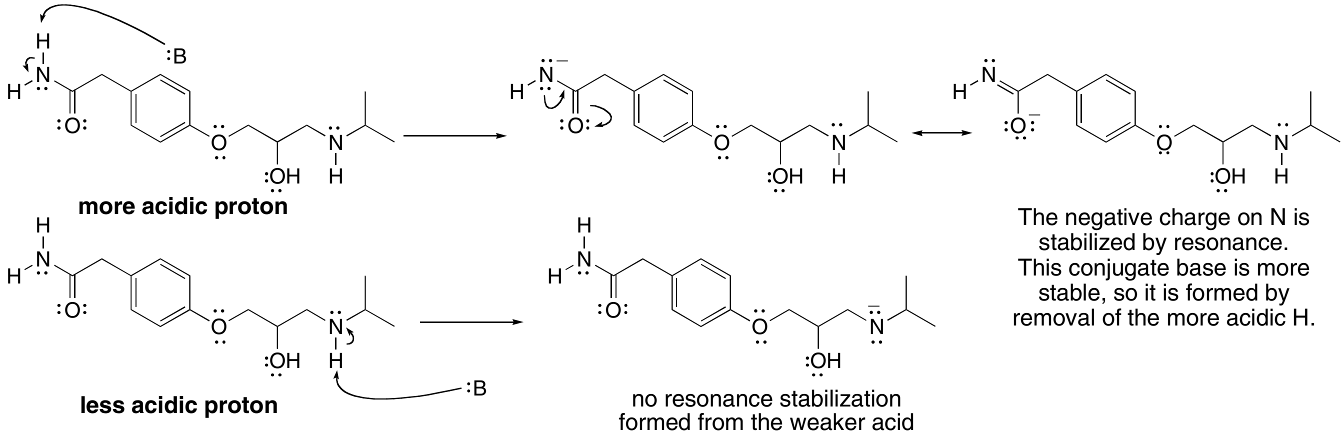


The negative charge is delocalized on the electronegative O atom. This stabilizes the conjugate base.

2.57 Compare the isomers.



2.58 Compare the Lewis structures of the conjugate bases when each H is removed. The more stable base makes the proton more acidic.



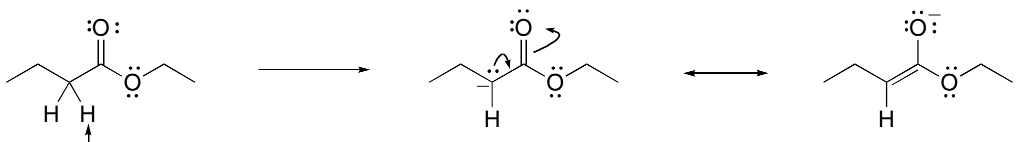
more acidic proton

less acidic proton

The negative charge on N is stabilized by resonance. This conjugate base is more stable, so it is formed by removal of the more acidic H.

no resonance stabilization formed from the weaker acid

2.59 Draw the conjugate base to determine the most acidic hydrogen.

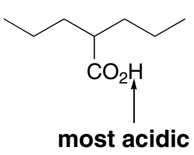


Resonance stabilization of the conjugate base makes this the most acidic proton. In Appendix A, the closest compound for comparison is $CH_3CO_2CH_2CH_3$ with a pK_a of 24.5; therefore, the estimated pK_a of ethyl butanoate is 25.

resonance-stabilized conjugate base

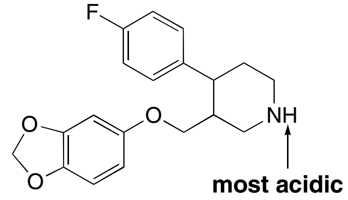
2.60 Look at the element bonded to the acidic H and decide its acidity based on the periodic trends. **Farther right across a row and down a column of the periodic table is more acidic.**

a.



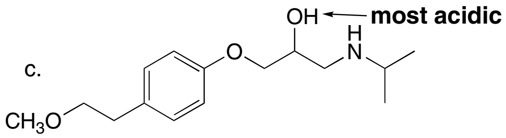
The molecule contains C–H and O–H bonds. O is farther right in the periodic table; therefore, the O–H hydrogen is the most acidic.

b.



The molecule contains C–H and N–H bonds. N is farther right in the periodic table; therefore, the N–H hydrogen is the most acidic.

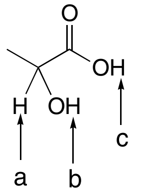
c.



The molecule contains C–H, N–H, and O–H bonds. O is farthest right in the periodic table; therefore, the O–H hydrogen is the most acidic.

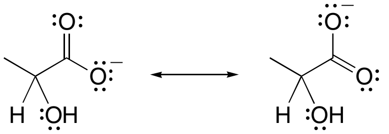
2.61 Use element effects, inductive effects, and resonance to determine which protons are the most acidic. The H's of the CH_3 group are least acidic since they are bonded to an *sp*^{3} hybridized C and the conjugate base formed by their removal is not resonance stabilized.

lactic acid



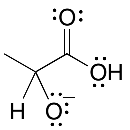
c > b > a
Both O–H protons [(b) and (c)] are more acidic than the C–H proton (a) by the element effect. The most acidic proton has added resonance stabilization when it is removed, making its conjugate base the most stable.

conjugate base by loss of (c):



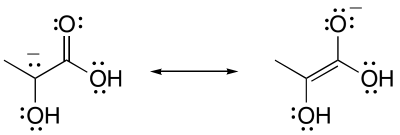
resonance stabilization
negative charge on O in both resonance structures
This makes (c) most acidic.

conjugate base by loss of (b):



no resonance stabilization, but
negative charge on O, an electronegative atom

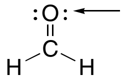
conjugate base by loss of (a):



This conjugate base has two resonance structures, but one places a negative charge on C.

2.62 ***Lewis bases* are electron pair donors**: they contain a lone pair or a π bond. ***Brønsted–Lowry bases* are proton acceptors**: to accept a proton they need a lone pair or a π bond. This means Lewis bases are also Brønsted–Lowry bases.

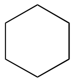
a.



lone pairs on O
both

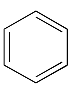
b. $CH_3-\ddot{Cl}:\leftarrow$ lone pairs on Cl
both

c.



neither = no lone pairs or π bond

d.



π bonds
both

2.63 **A *Lewis acid* is an electron pair acceptor** and usually contains a proton or an unfilled valence shell of electrons. A ***Brønsted–Lowry acid* is a proton donor** and must contain a hydrogen atom. All Brønsted–Lowry acids are Lewis acids, though the reverse may not be true.

a. H_3O^+
both - contains a H

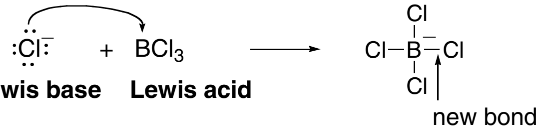
b. Cl_3C^+
Lewis acid - unfilled valence shell on C

c. BCl_3
Lewis acid - unfilled valence shell on B

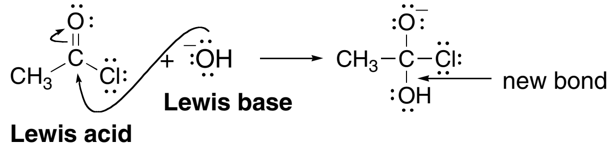
d. BF_4^-
neither - no H or unfilled valence shell

2.64 Label the Lewis acid and Lewis base and then draw the products.

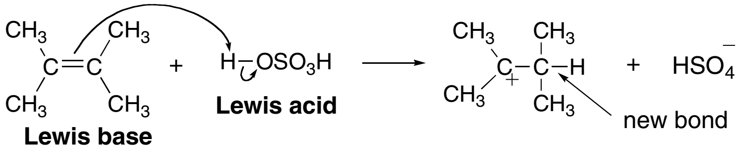
a.



c.

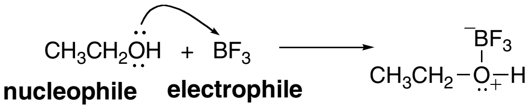


b.

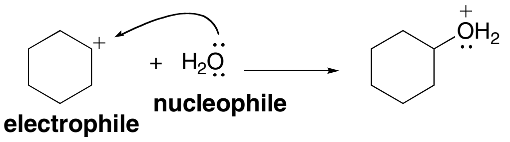


2.65 A Lewis acid is also called an **electrophile**. When a Lewis base reacts with an electrophile other than a proton, it is called a **nucleophile**. Label the electrophile and nucleophile in the starting materials and then draw the products.

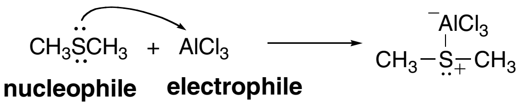
a.



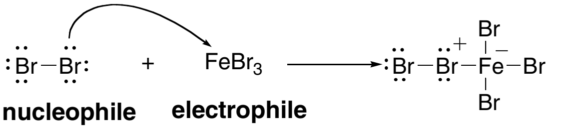
d.



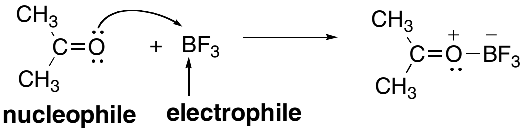
b.



e.

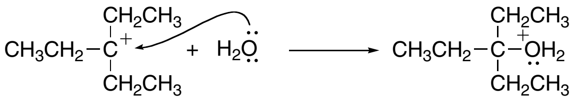


c.

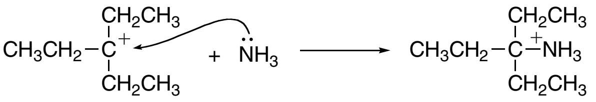


2.66 Draw the product of each reaction.

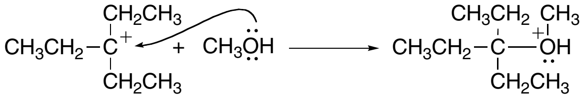
a.



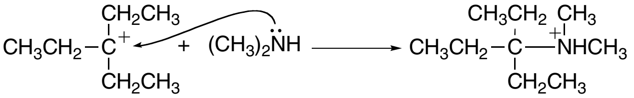
d.



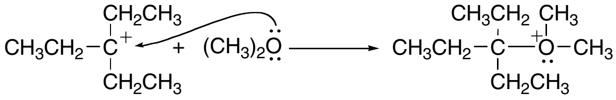
b.



e.

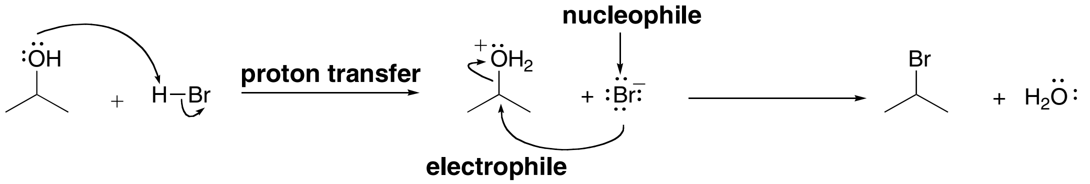


c.

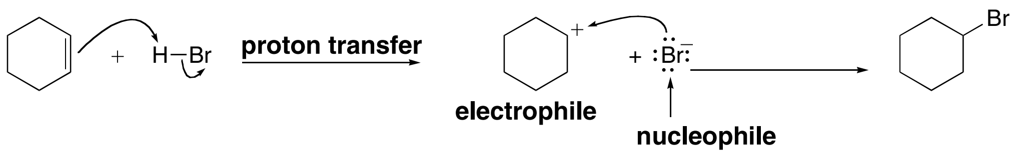


2.67

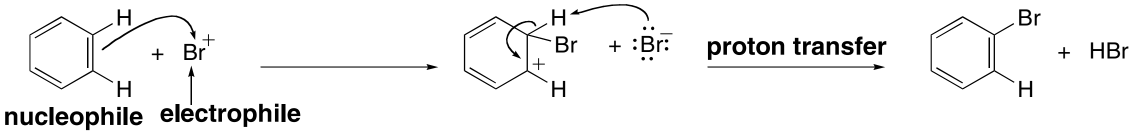
a.



b.

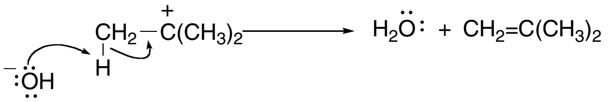


c.

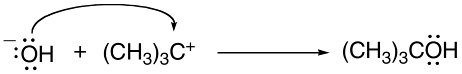


2.68 Draw the products of each reaction. In part (a), ⁻OH pulls off a proton and thus acts as a Brønsted–Lowry base. In part (b), ⁻OH attacks a carbon and thus acts as a Lewis base.

a.

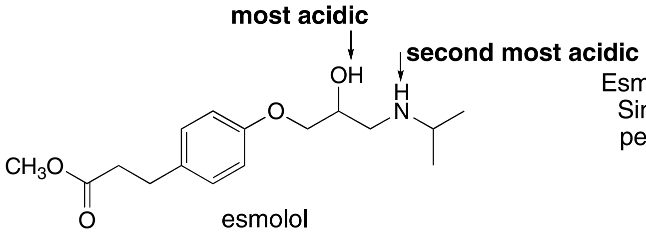


b.



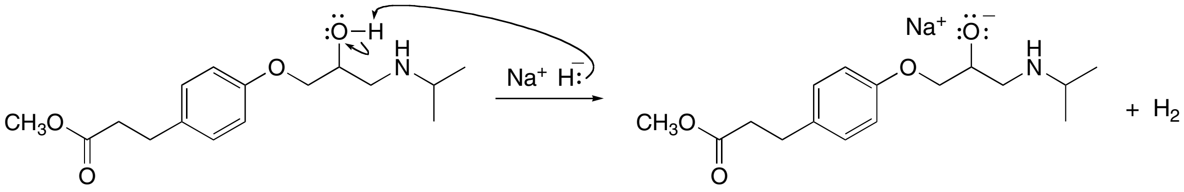
2.69 Answer each question about esmolol.

a.

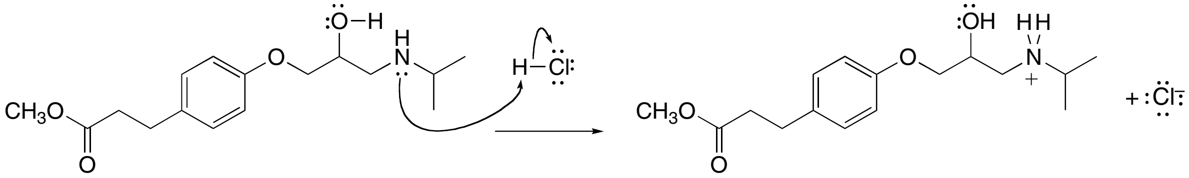


Esmolol contains C–H, N–H, and O–H bonds. Since acidity increases across a row of the periodic table, the OH bond is most acidic, followed by the NH bond.

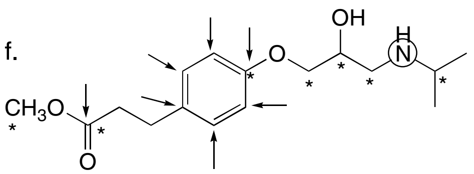
b.



c.

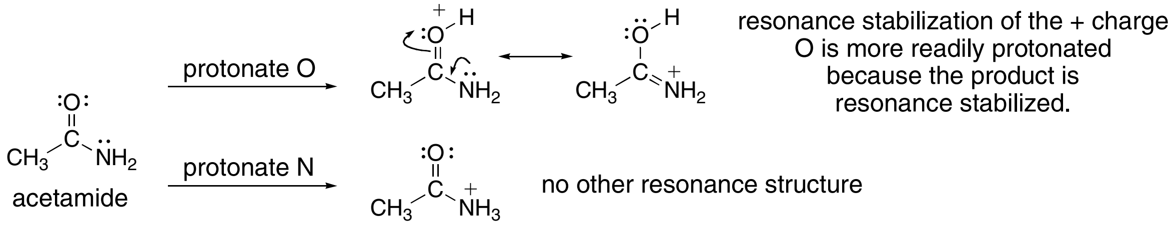


d, e, f.



All sp^2 C are indicated with an arrow.
The N is the only trigonal pyramidal atom.
The δ^+ C's are indicated with a (*).

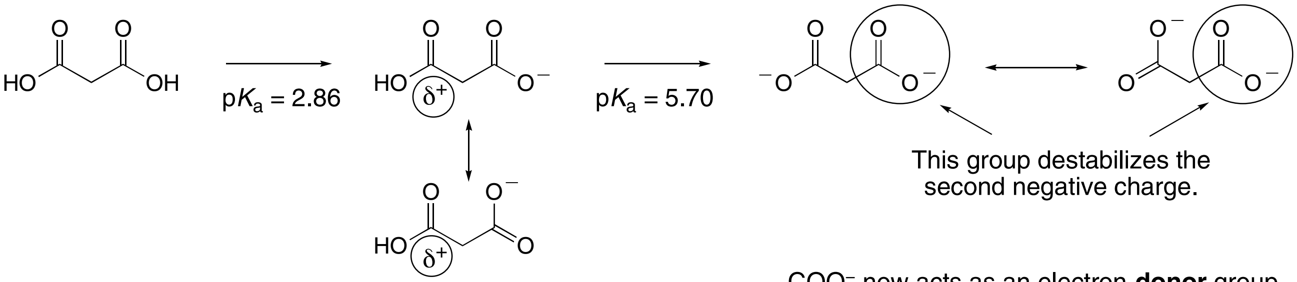
2.70 Draw the product of protonation of either O or N and compare the conjugate acids. When acetamide reacts with an acid, the O atom is protonated because it results in a resonance-stabilized conjugate acid.



resonance stabilization of the + charge
O is more readily protonated
because the product is
resonance stabilized.

no other resonance structure

2.71



This group destabilizes the second negative charge.

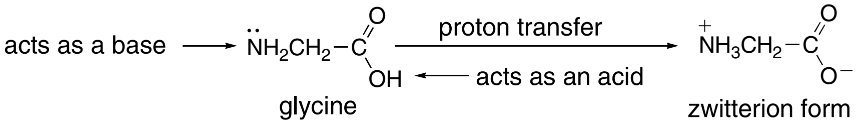
δ$^+$ stabilizes the (–) charge of the conjugate base.

The nearby COOH group serves as an electron-**withdrawing** group to stabilize the negative charge. This makes the first proton **more** acidic than CH_3COOH.

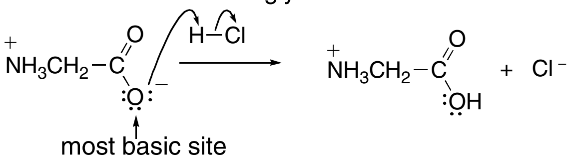
COO^- now acts as an electron-**donor** group which destabilizes the conjugate base, making removal of the second proton more difficult and thus it is **less** acidic than CH_3COOH.

2.72 The COOH group of glycine gives up a proton to the basic NH_2 group to form the zwitterion.

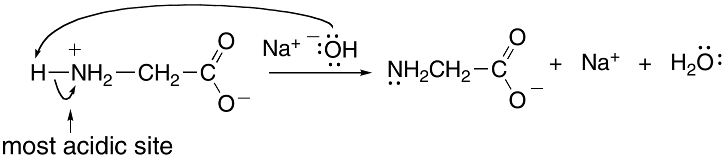
a.



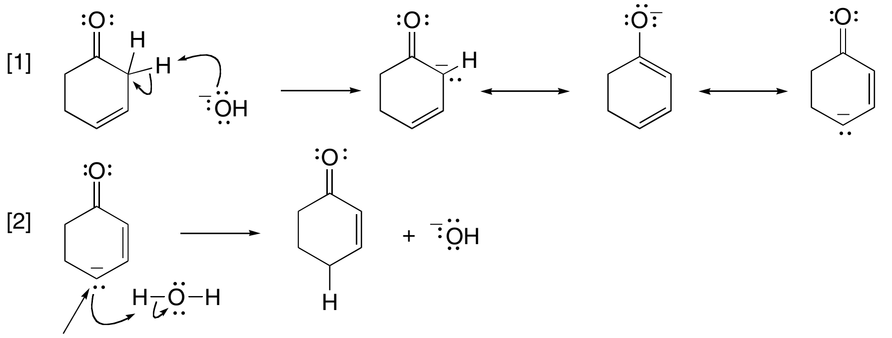
b.



c.

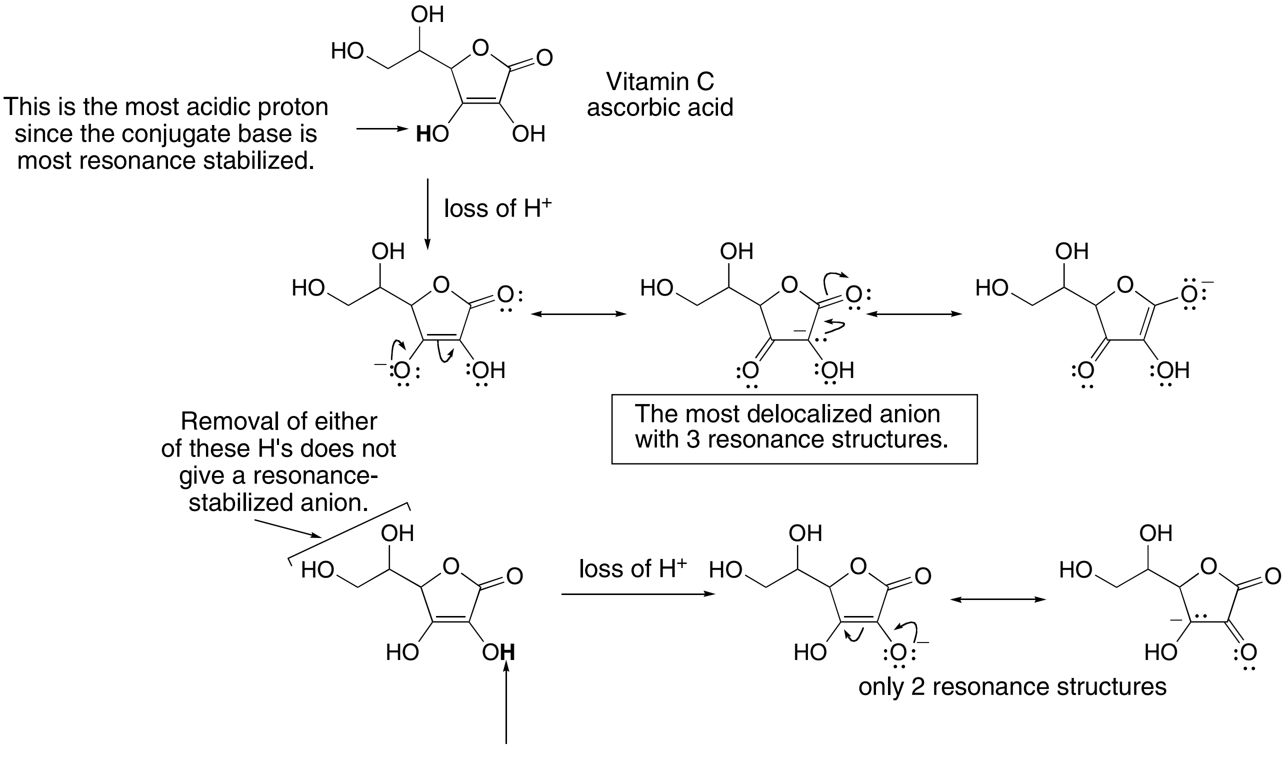


2.73 Use curved arrows to show how the reaction occurs.



Protonate the negative charge on this carbon to form the product.

2.74 Compare the OH bonds in Vitamin C and decide which one is the most acidic.



Vitamin C
ascorbic acid

This is the most acidic proton since the conjugate base is most resonance stabilized.

The most delocalized anion with 3 resonance structures.

Removal of either of these H's does not give a resonance-stabilized anion.

only 2 resonance structures

This proton is less acidic since its conjugate base is less resonance stabilized.