Chapter 19: Carboxylic Acids and the Acidity of the O–H Bond

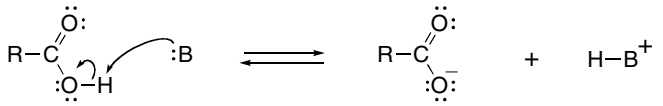
♦ General facts

- Carboxylic acids contain a carboxy group (COOH). The central carbon is sp^2 hybridized and trigonal planar (19.1).
- Carboxylic acids are identified by the suffixes *-oic acid*, *carboxylic acid*, or *-ic acid* (19.2).
- Carboxylic acids are polar compounds that exhibit hydrogen bonding interactions (19.3).

♦ Summary of spectroscopic absorptions (19.4)

IR absorptions	C=O	~1710 cm^{-1}
	O–H	3500–2500 cm^{-1} (very broad and strong)
^{1}H NMR absorptions	O–H	10–12 ppm (highly deshielded proton)
	C–H α to COOH	2–2.5 ppm (somewhat deshielded Csp^3–H)
^{13}C NMR absorption	C=O	170–210 ppm (highly deshielded carbon)

♦ General acid–base reaction of carboxylic acids (19.9)

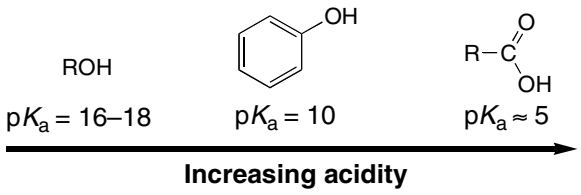


p$K_a \approx 5$ carboxylate anion

- Carboxylic acids are especially acidic because carboxylate anions are resonance stabilized.
- For equilibrium to favor the products, the base must have a conjugate acid with a p$K_a > 5$. Common bases are listed in Table 19.3.

♦ Factors that affect acidity

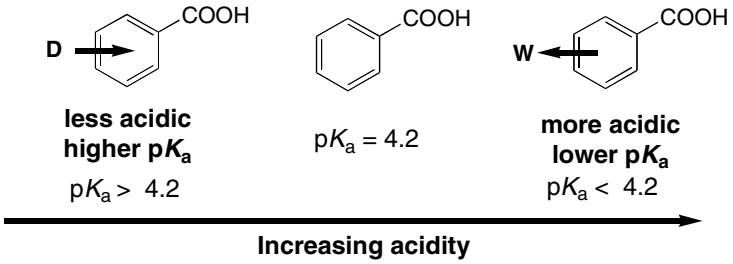
Resonance effects. A carboxylic acid is more acidic than an alcohol or phenol because its conjugate base is more effectively stabilized by resonance (19.9).



Inductive effects. Acidity increases with the presence of electron-withdrawing groups (like the electronegative halogens) and decreases with the presence of electron-donating groups (like polarizable alkyl groups) (19.10).

Substituted benzoic acids.

- Electron-donor groups (D) make a substituted benzoic acid less acidic than benzoic acid.
- Electron-withdrawing groups (W) make a substituted benzoic acid more acidic than benzoic acid.

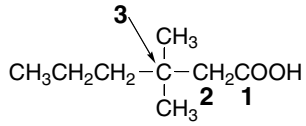


♦ Other facts

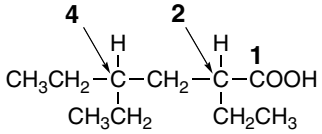
- Extraction is a useful technique for separating compounds having different solubility properties. Carboxylic acids can be separated from other organic compounds by extraction, because aqueous base converts a carboxylic acid into a water-soluble carboxylate anion (19.12).
- A sulfonic acid (RSO_3H) is a strong acid because it forms a weak, resonance-stabilized conjugate base on deprotonation (19.13).
- Amino acids have an amino group on the α carbon to the carboxy group [$RCH(NH_2)COOH$]. Amino acids exist as zwitterions at pH ≈ 6. Adding acid forms a species with a net (+1) charge [$RCH(NH_3)COOH]^+$. Adding base forms a species with a net (–1) charge [$RCH(NH_2)COO]^-$ (19.14).

Chapter 19: Answers to Problems

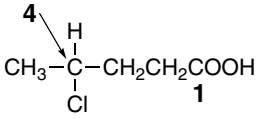
19.1 To name a carboxylic acid:
[1] Find the longest chain containing the COOH group and change the *-e* ending to *-oic acid*.
[2] Number the chain to put the COOH carbon at C1, but omit the number from the name.
[3] Follow all other rules of nomenclature.

a. 

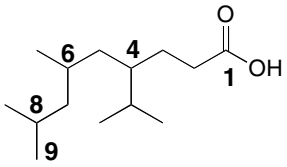
Number the chain to put COOH at C1.
6 carbon chain = **hexanoic acid**
3,3-dimethylhexanoic acid

c. 

Number the chain to put COOH at C1.
6 carbon chain = **hexanoic acid**
2,4-diethylhexanoic acid

b. 

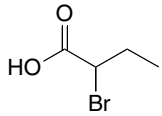
Number the chain to put COOH at C1.
5 carbon chain = **pentanoic acid**
4-chloropentanoic acid

d. 

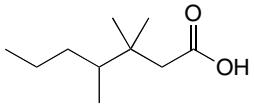
Number the chain to put COOH at C1.
9 carbon chain = **nonanoic acid**
4-isopropyl-6,8-dimethylnonanoic acid

19.2

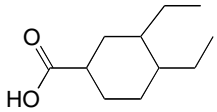
a. 2-bromo**butanoic acid**



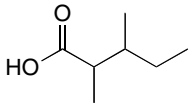
c. 3,3,4-trimethyl**heptanoic acid**



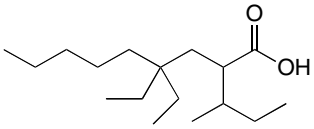
e. 3,4-diethyl**cyclohexanecarboxylic acid**



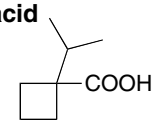
b. 2,3-dimethyl**pentanoic acid**



d. 2-*sec*-butyl-4,4-diethyl**nonanoic acid**

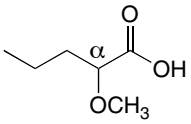


f. 1-isopropyl**cyclobutane-carboxylic acid**

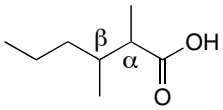


19.3

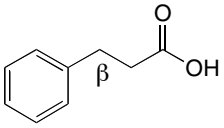
a. α-methoxy**valeric acid**



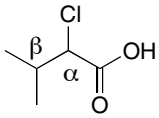
c. α,β-dimethyl**caproic acid**



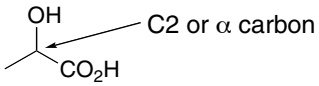
b. β-phenyl**propionic acid**



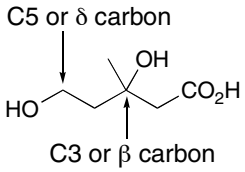
d. α-chloro-β-methyl**butyric acid**



19.4

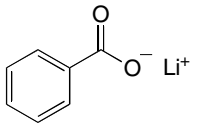
a. 

IUPAC: 2-hydroxy**propanoic acid**
common: α-hydroxy**propionic acid**

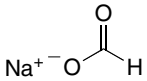
b. 

IUPAC: 3,5-dihydroxy-3-methyl**pentanoic acid**
common: β,δ-dihydroxy-β-methyl**valeric acid**

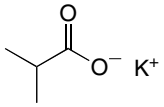
19.5

a. 

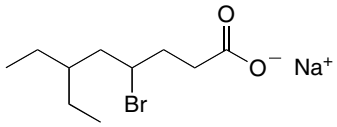
lithium benzoate

b. 

sodium formate
or
sodium methanoate

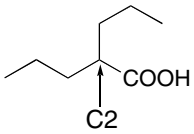
c. 

potassium 2-methylpropanoate

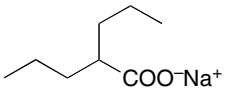
d. 

sodium 4-bromo-6-ethyl-octanoate

19.6

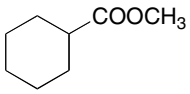


2-propyl**pentanoic acid**

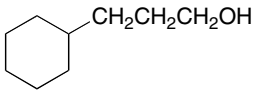


sodium 2-propyl**pentanoate**

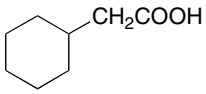
19.7 More polar molecules have a higher boiling point and are more water soluble.



least polar
lowest boiling point
least H_2O soluble

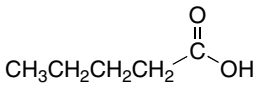


intermediate polarity
intermediate boiling point

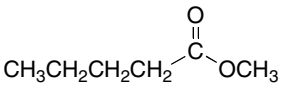


most polar
highest boiling point
most H_2O soluble

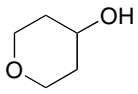
19.8 Look for functional group differences to distinguish the compounds by IR. Besides sp^3 hybridized C–H bonds at 3000–2850 cm^{-1} (which all three compounds have), the following functional group absorptions are seen:



carboxylic acid
2 strong absorptions
~1710 (C=O)
~2500–3500 (OH) cm^{-1}



ester
1 strong absorption
~1700 (C=O) cm^{-1}

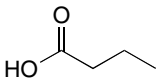


alcohol
1 strong absorption
~3600–3200 (OH) cm^{-1}

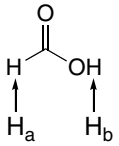
19.9

Molecular formula: $C_4H_8O_2$
one degree of unsaturation

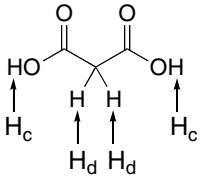
^{1}H NMR data (ppm):
0.95 (triplet, 3 H)
1.65 (multiplet, 2 H)
2.30 (triplet, 2 H)
11.8 (singlet, 1 H)



19.10



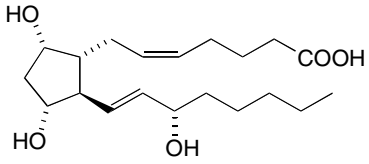
2 singlets
1:1 ratio



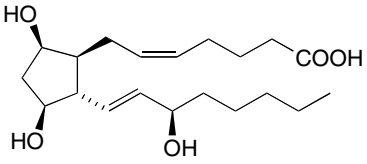
2 singlets
1:1 ratio

Although both compounds have an absorption at 10–12 ppm in their ^{1}H NMR spectra (due to H_b and H_c), H_a, which is bonded directly to the carbonyl carbon, is much farther downfield than H_d because it is more deshielded.

19.11



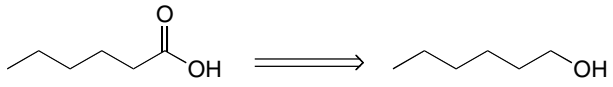
$PGF_{2\alpha}$
a prostaglandin

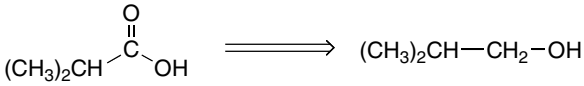


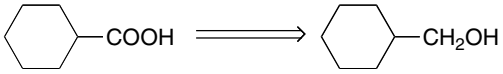
enantiomer

There are five tetrahedral stereogenic centers. Both double bonds can exhibit cis–trans isomerism. Therefore, there are $2^7 = 128$ stereoisomers.

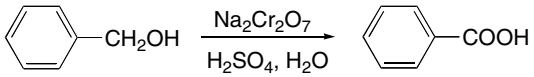
19.12 1° Alcohols are converted to carboxylic acids by oxidation reactions.

a. 

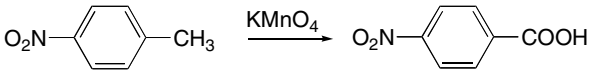
b. 

c. 

19.13

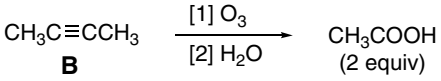
a. 

A

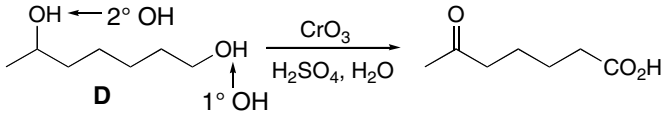
c. 

C

(Any R group with benzylic H's can be present para to NO_2.)

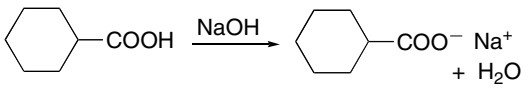
b. 

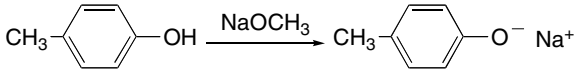
B

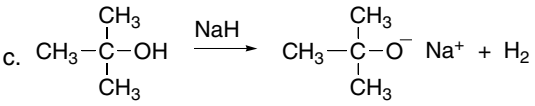
d. 

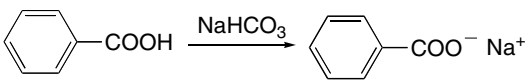
D

19.14

a. 

b. 

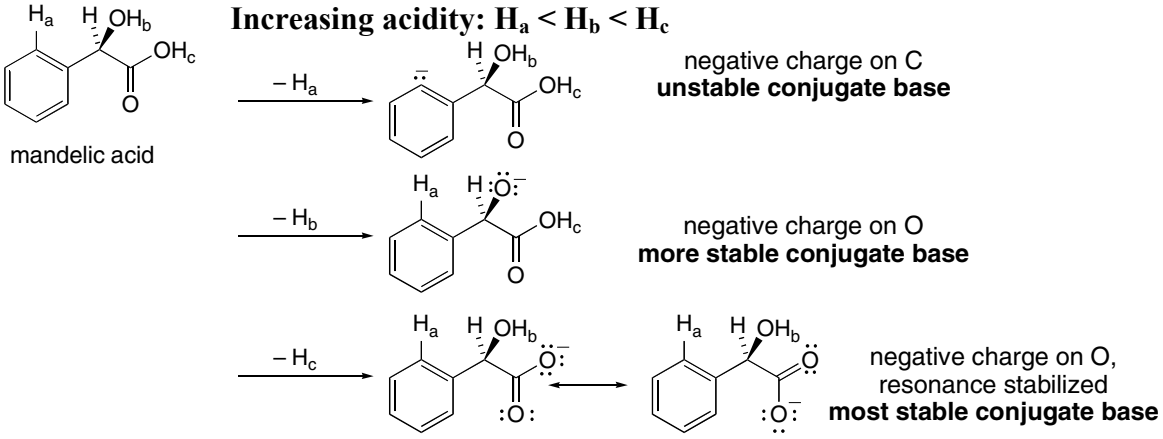
c. 

d. 

19.15 CH_3COOH has a pK_a of 4.8. Any base with a conjugate acid with a pK_a higher than 4.8 can deprotonate it.

a. F^- pK_a (HF) = 3.2 **not strong enough**
b. $(CH_3)_3CO^-$ pK_a [$(CH_3)_3COH$]= 18 **strong enough**
c. CH_3^- pK_a (CH_4) = 50 **strong enough**
d. $^-NH_2$ pK_a (NH_3) = 38 **strong enough**
e. Cl^- pK_a (HCl) = –7.0 **not strong enough**

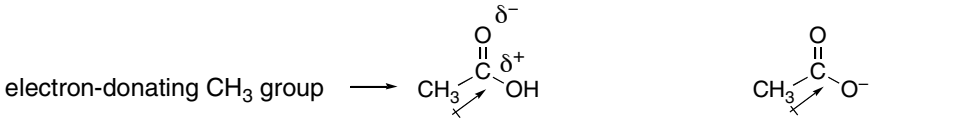
19.16



19.17 Electron-withdrawing groups make an acid more acidic, lowering its pK_a.

CH_3CH_2-COOH	ICH_2-COOH	CF_3-COOH
least acidic	one electron-withdrawing group	three electron-withdrawing F's
pK_a = 4.9	intermediate acidity	most acidic
	pK_a = 3.2	pK_a = 0.2

19.18 Acetic acid has an electron-donating methyl group bonded to the carboxy group. The CH_3 group both stabilizes the acid and destabilizes the nearby negative charge on the conjugate base, making CH_3COOH less acidic (with a higher pK_a) than HCOOH.



acetic acid
CH_3 stabilizes the partial positive charge.

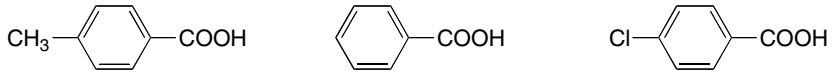
conjugate base
CH_3 destabilizes the negative charge.
a less stable conjugate base

19.19

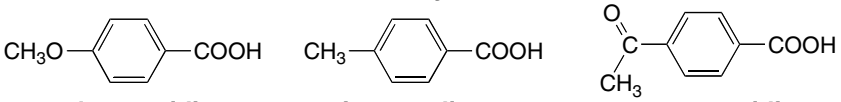
a. CH_3COOH **least acidic** | $HSCH_2COOH$ **intermediate acidity** | $HOCH_2COOH$ **most acidic**

b. ICH_2CH_2COOH **least acidic** | ICH_2COOH **intermediate acidity** | $I_2CHCOOH$ **most acidic**

19.20

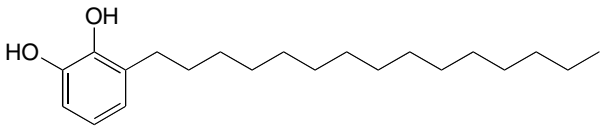
a. 

least acidic | **intermediate acidity** | **most acidic**

b. 

least acidic | **intermediate acidity** | **most acidic**

19.21



A

Phenol **A** has a higher pK_a than phenol because of its substituents. Both the OH and CH_3 are electron-donating groups, which make the conjugate base less stable. Therefore, the acid is **less acidic.**

19.22 To separate compounds by an extraction procedure, they must have different solubility properties.

a. $CH_3(CH_2)_6COOH$ and $CH_3CH_2CH_2CH_2CH{=}CH_2$: **YES**. The acid can be extracted into aqueous base, while the alkene will remain in an organic layer.

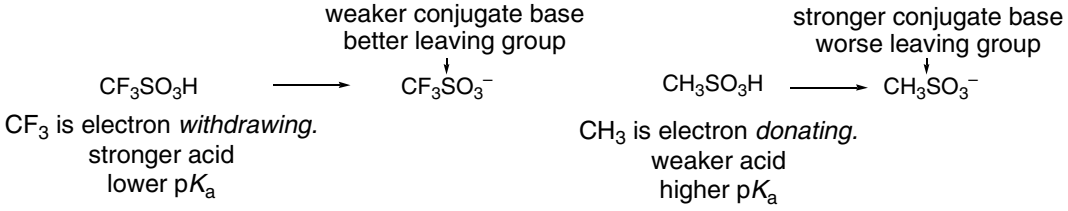
b. $CH_3CH_2CH_2CH_2CH{=}CH_2$ and $(CH_3CH_2CH_2)_2O$: **NO.** Both compounds are soluble in organic solvents and insoluble in water. Neither is acidic enough to be extracted into aqueous base.

c. $CH_3(CH_2)_6COOH$ and NaCl: one carboxylic acid, one salt: **YES.** The carboxylic acid is soluble in an organic solvent while the salt is soluble in water.

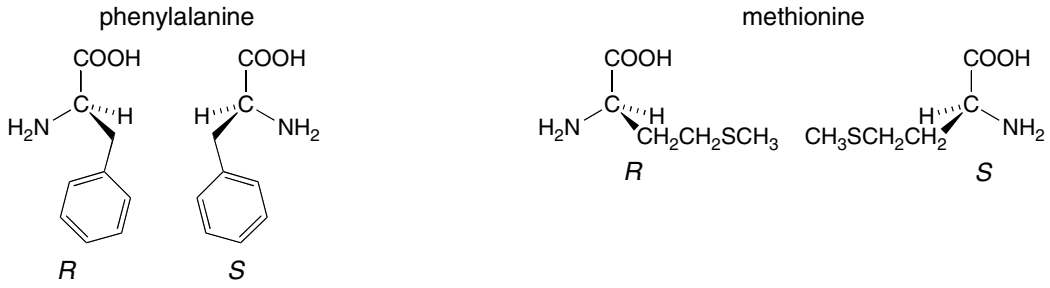
d. NaCl and KCl: two salts: **NO.**

19.23 To separate compounds by an aqueous extraction technique, compounds must have different solubility properties. CH_3CH_2COOH and $CH_3CH_2CH_2OH$ are low molecular weight organic compounds that can hydrogen bond to water, so they are water soluble. They also both dissolve in organic solvents. As a result, they are inseparable because of their similar solubility properties.

19.24

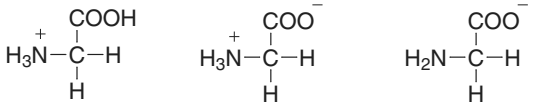


19.25



19.26 Since amino acids exist as zwitterions (i.e., salts), they are too polar to be soluble in organic solvents like diethyl ether. Thus, they are soluble in water.

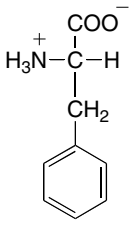
19.27



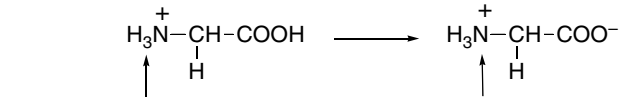
pH = 1 glycine neutral form pH = 11

19.28

$$pI = \frac{pK_a(COOH) + pK_a(NH_3^+)}{2} = \frac{(2.58) + (9.24)}{2} = 5.91$$



19.29



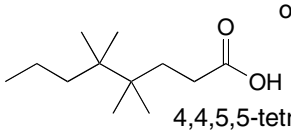
electron-withdrawing group

The nearby (+) stabilizes the conjugate base by an electron-withdrawing inductive effect, thus making the starting acid more acidic.

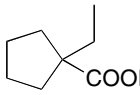
19.30 Use the directions from Answer 19.1 to name the compounds.

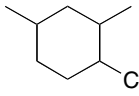
a. $(CH_3)_2CHCH_2CH_2CO_2H$ 4-methylpentanoic acid

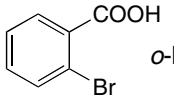
b. $BrCH_2COOH$ 2-bromoacetic acid or 2-bromoethanoic acid

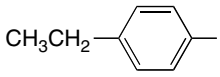
c. 
4,4,5,5-tetramethyloctanoic acid

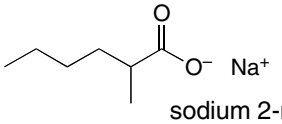
d. $CH_3CH_2CH_2COO^-Li^+$ lithium butanoate

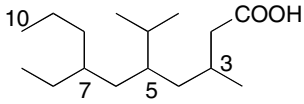
e. 
1-ethylcyclopentanecarboxylic acid

f. 
2,4-dimethylcyclohexanecarboxylic acid

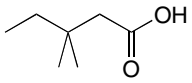
g. 
o-bromobenzoic acid

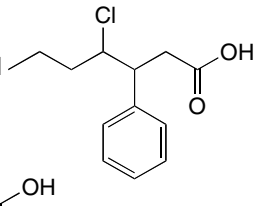
h. 
p-ethylbenzoic acid

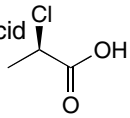
i. 
sodium 2-methylhexanoate

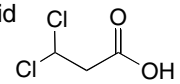
j. 
7-ethyl-5-isopropyl-3-methyldecanoic acid

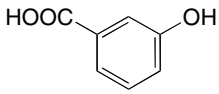
19.31

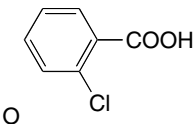
a. 3,3-dimethylpentanoic acid 

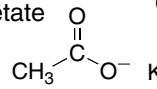
b. 4-chloro-3-phenylheptanoic acid 

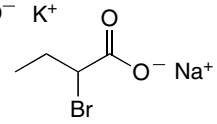
c. (2*R*)-2-chloropropanoic acid 

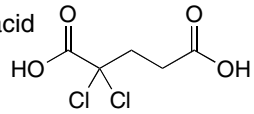
d. β,β-dichloropropionic acid 

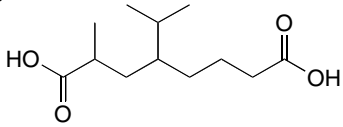
e. *m*-hydroxybenzoic acid 

f. *o*-chlorobenzoic acid 

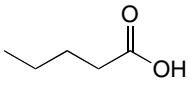
g. potassium acetate 

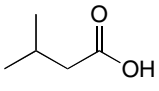
h. sodium α-bromobutyrate 

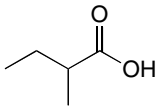
i. 2,2-dichloropentanedioic acid 

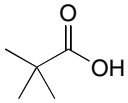
j. 4-isopropyl-2-methyloctanedioic acid 

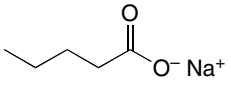
19.32

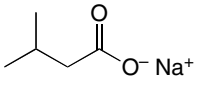

pentanoic acid

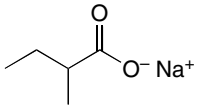

3-methylbutanoic acid

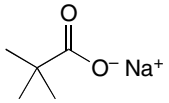

2-methylbutanoic acid


2,2-dimethylpropanoic acid

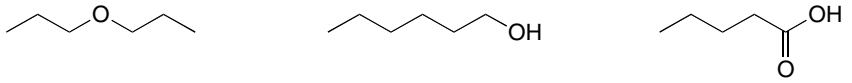

sodium pentanoate


sodium 3-methylbutanoate

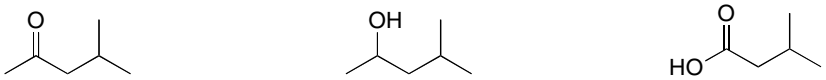

sodium 2-methylbutanoate


sodium 2,2-dimethylpropanoate

19.33

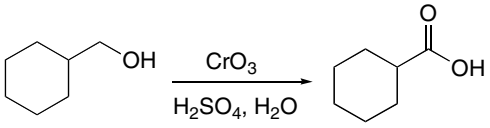
a. 

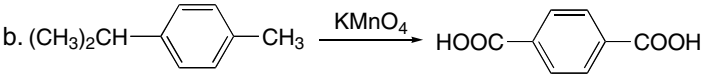
lowest boiling point **intermediate boiling point** **highest boiling point**

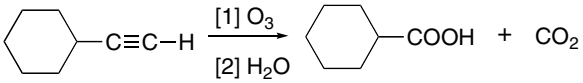
b. 

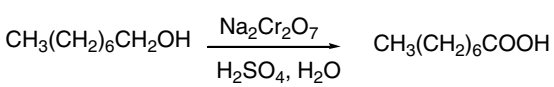
lowest boiling point **intermediate boiling point** **highest boiling point**

19.34

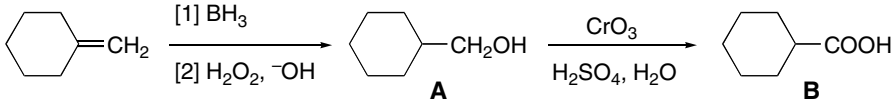
a. 

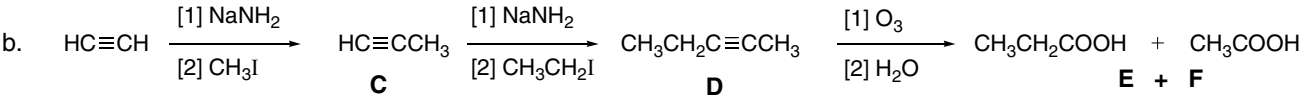
b. 

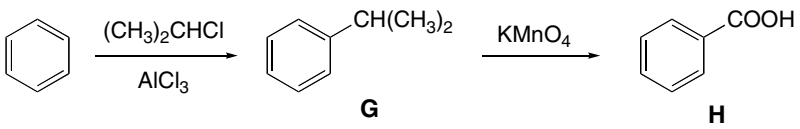
c. 

d. 

19.35

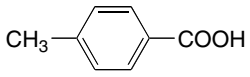
a. 

b. 

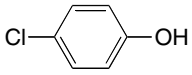
c. 

19.36

Bases: [1] $^{-}$OH pK_a (H_2O) = 15.7; [2] $CH_3CH_2^-$ pK_a (CH_3CH_3) = 50; [3] $^{-}NH_2$ pK_a (NH_3) = 38; [4] NH_3 pK_a (NH_4^+) = 9.4; [5] $HC{\equiv}C^-$ pK_a ($HC{\equiv}CH$) = 25.

a. 

pK_a = 4.3
All of the bases can deprotonate this.

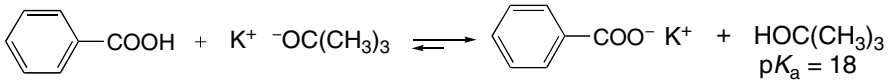
b. 

pK_a = 9.4
$^{-}$OH, $CH_3CH_2^-$, $^{-}NH_2$, and $HC{\equiv}C^-$ can deprotonate this.

c. $(CH_3)_3COH$

pK_a = 18
$CH_3CH_2^-$, $^{-}NH_2$, and $HC{\equiv}C^-$ can deprotonate this.

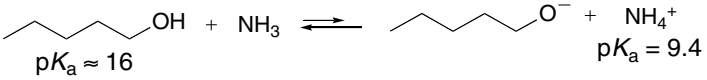
19.37

a. 

pK_a = 4.2

pK_a = 18

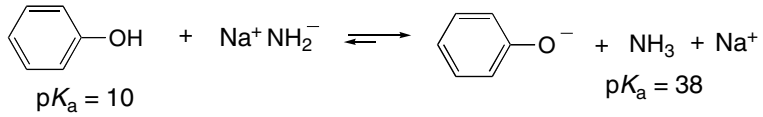
Reaction favors products.

b. 

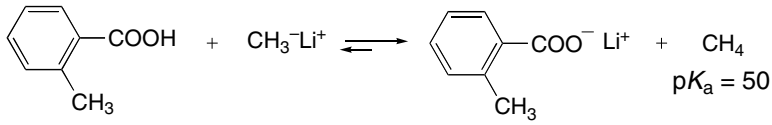
p$K_a \approx$ 16

pK_a = 9.4

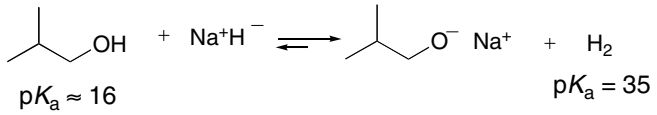
Reaction favors reactants.

c. 

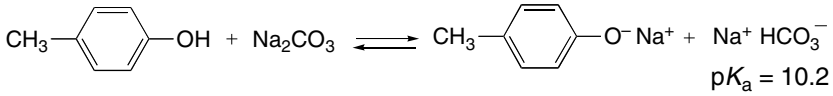
pK_a = 10 pK_a = 38 Reaction favors products.

d. 

p$K_a \approx 4$ pK_a = 50 Reaction favors products.

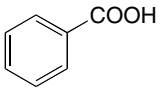
e. 

p$K_a \approx 16$ pK_a = 35 Reaction favors products.

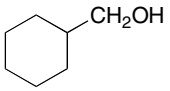
f. 

pK_a = 10.2 pK_a = 10.2 With the same pK_a for the starting acid and the conjugate acid, an equal amount of starting materials and products is present.

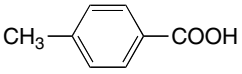
19.38 The stronger acid has a lower pK_a and a weaker conjugate base.

a. 

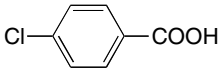
carboxylic acid
stronger acid
lower pK_a
weaker conjugate base

or 

alcohol
weaker acid
higher pK_a
stronger conjugate base

c. 

CH_3 is electron donating.
weaker acid
higher pK_a
stronger conjugate base

or 

Cl is electron withdrawing.
stronger acid
lower pK_a
weaker conjugate base

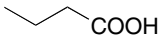
b. $ClCH_2COOH$
weaker acid
higher pK_a
stronger conjugate base

or FCH_2COOH
F is more electronegative.
stronger acid
lower pK_a
weaker conjugate base

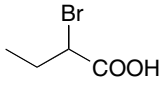
d. $NCCH_2COOH$
CN is electron withdrawing.
stronger acid
lower pK_a
weaker conjugate base

or CH_3COOH
weaker acid
higher pK_a
stronger conjugate base

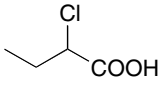
19.39

a. 

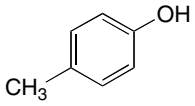
least acidic



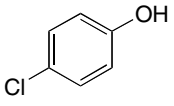
Br is electronegative
intermediate acidity



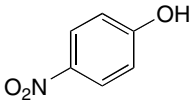
Cl more electronegative
most acidic

b. 

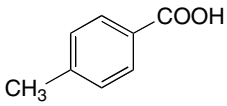
least acidic



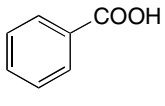
intermediate acidity



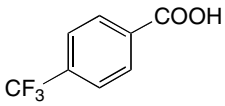
most acidic

c. 

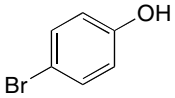
least acidic



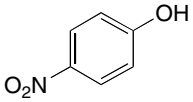
intermediate acidity



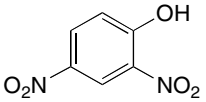
most acidic

d. 

least acidic



intermediate acidity



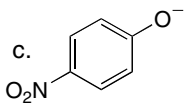
most acidic

19.40

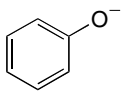
a. $BrCH_2COO^-$ $BrCH_2CH_2COO^-$ $(CH_3)_3CCOO^-$

weakest base **intermediate basicity** **strongest base**

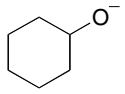
c.



weakest base

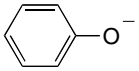


intermediate basicity

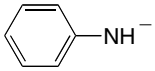


strongest base

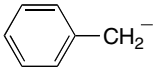
b.



weakest base



intermediate basicity



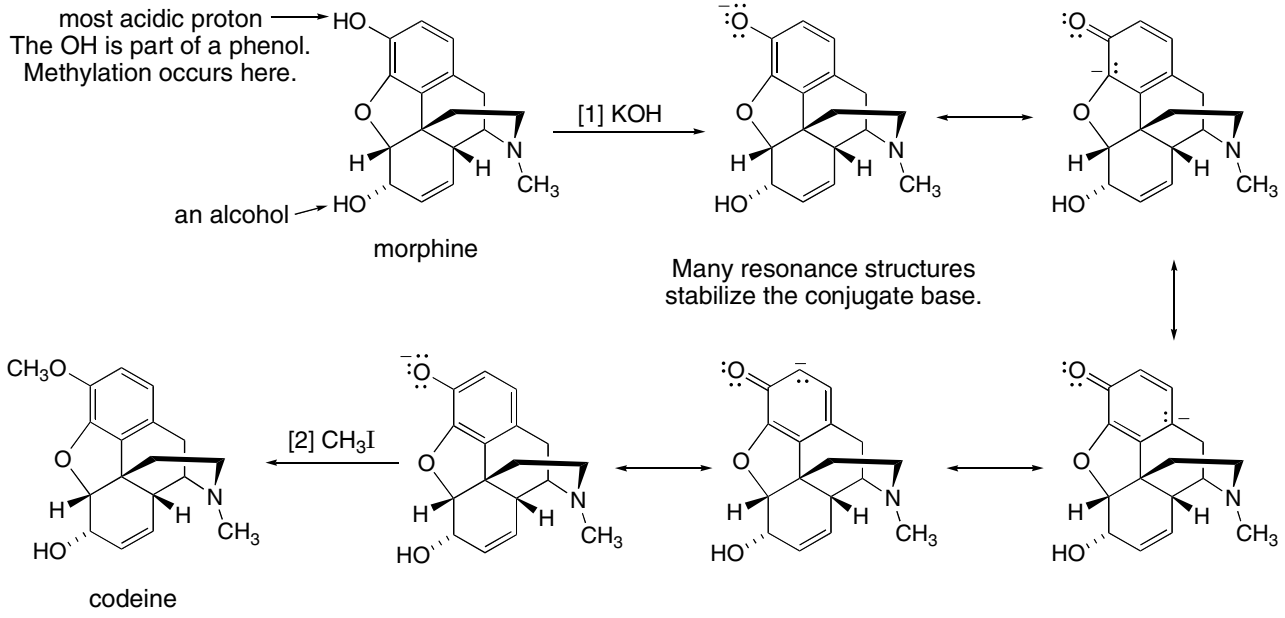
strongest base

19.41

Increasing acidity →

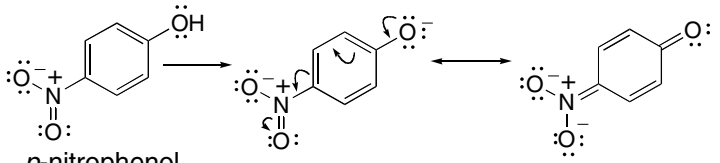
	ICH_2COOH	$BrCH_2COOH$	FCH_2COOH	$F_2CHCOOH$	F_3CCOOH
pK_a values	least acidic 3.12	2.86	2.66	1.24	most acidic 0.28

19.42 The OH of the phenol group in morphine is more acidic than the OH of the alcohol (p$K_a \approx 10$ versus p$K_a \approx 16$). KOH is basic enough to remove the phenolic OH, the most acidic proton.



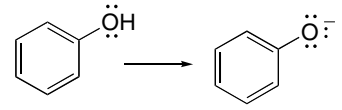
19.43

a. The negative charge on the conjugate base of *p*-nitrophenol is delocalized on the NO_2 group, stabilizing the conjugate base, and making *p*-nitrophenol more acidic than phenol (where the negative charge is delocalized only around the benzene ring).



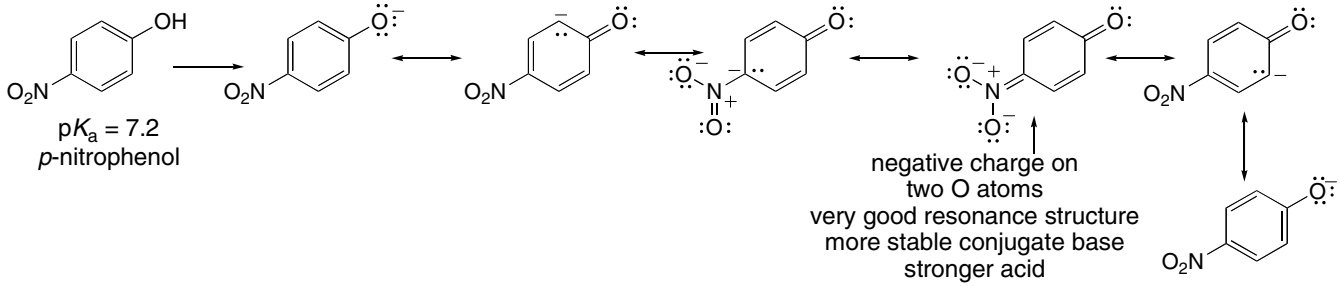
p-nitrophenol
pK_a = 7.2

two of the possible resonance structures for the conjugate base (See part b. for all the possible resonance structures.)



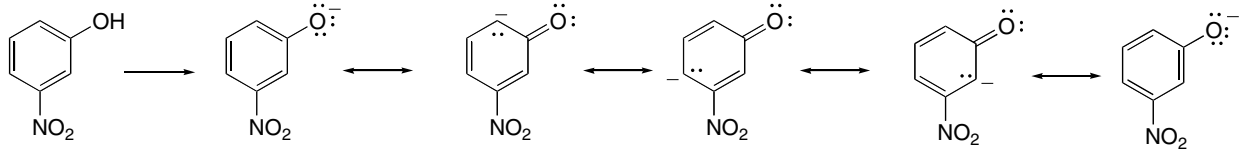
phenol
pK_a = 10

b. In the para isomer, the negative charge of the conjugate base is delocalized over both the benzene ring and onto the NO_2 group, whereas in the meta isomer it cannot be delocalized onto the NO_2 group. This makes the conjugate base from the para isomer more highly resonance stabilized, and the para substituted phenol more acidic than its meta isomer.



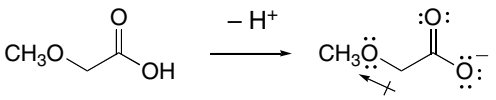
pK_a = 7.2
p-nitrophenol

negative charge on two O atoms
very good resonance structure
more stable conjugate base
stronger acid



pK_a = 8.3
m-nitrophenol

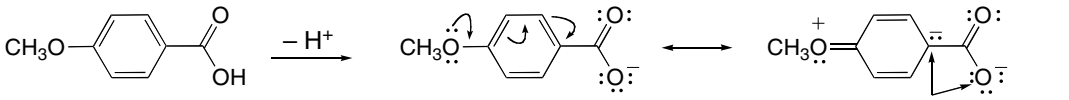
19.44 A CH_3O group has an electron-withdrawing inductive effect and an electron-donating resonance effect. In 2-methoxyacetic acid, the OCH_3 group is bonded to an sp^3 hybridized C, so there is no way to donate electron density by resonance. The CH_3O group withdraws electron density because of the electronegative O atom, stabilizing the conjugate base, and making CH_3OCH_2COOH a stronger acid than CH_3COOH.



more acidic acid

more stable conjugate base

In *p*-methoxybenzoic acid, the CH_3O group is bonded to an sp^2 hybridized C, so it can donate electron density by a resonance effect. This destabilizes the conjugate base, making the starting material less acidic than C_6H_5COOH.

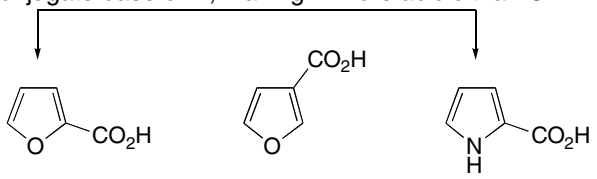


less acidic acid

like charges nearby
less stable conjugate base

19.45

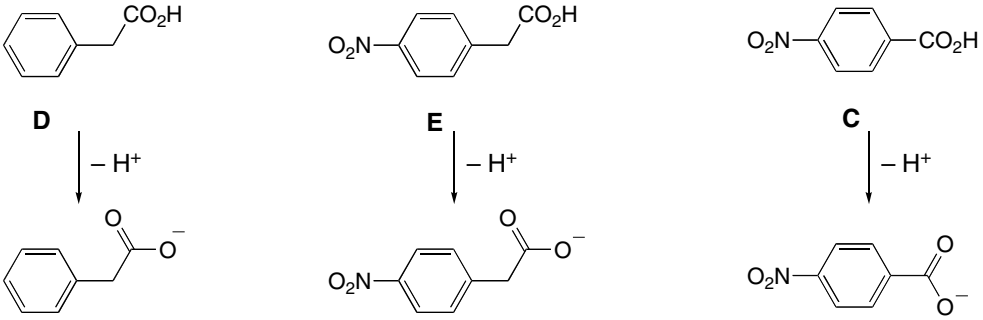
The O in **A** is more electronegative than the N in **C** so there is a stronger electron-withdrawing inductive effect. This stabilizes the conjugate base of **A**, making **A** more acidic than **C**.



A $pK_a = 3.2$ **B** $pK_a = 3.9$ **C** $pK_a = 4.4$

Since the O in **A** is closer to the COOH group than the O atom in **B**, there is a stronger electron-withdrawing inductive effect. This makes **A** more acidic than **B**.

19.46

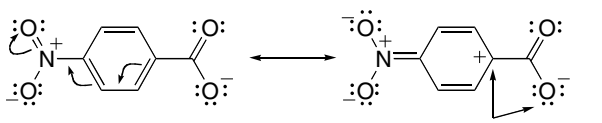


Since the benzene ring is bonded to the α carbon (not the carbonyl carbon), this compound is not much different than any alkyl-substituted carboxylic acid.
least acidic

The electron withdrawing-inductive effect of the NO_2 group helps stabilize the COO^- group.
intermediate acidity

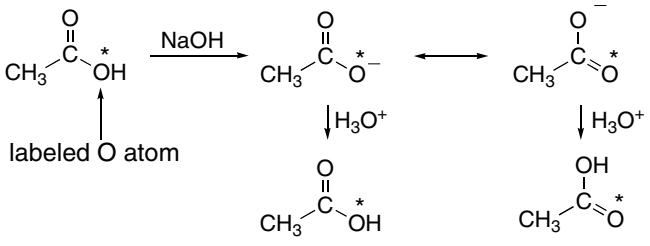
Since the NO_2 group is bonded to a benzene ring that is bonded directly to the carbonyl group, inductive effects and resonance effects stabilize the conjugate base. For example, a resonance structure can be drawn that places a (+) charge close to the COO^- group.
most acidic

Two of the resonance structures for the conjugate base of **C**:



unlike charges nearby
stabilizing

19.47

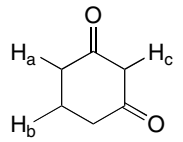


The resonance-stabilized carboxylate anion can now be protonated on either O atom, the one with the label and the one without the label.

The label is now in two different locations.

19.48

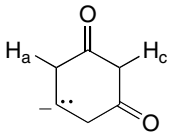
a.



1,3-cyclohexanedione

increasing acidity: $H_b < H_a < H_c$

loss of H_b:

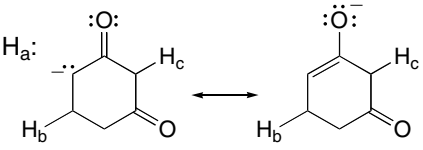


one Lewis structure

least stable conjugate base

The most acidic proton forms the most stable conjugate base.

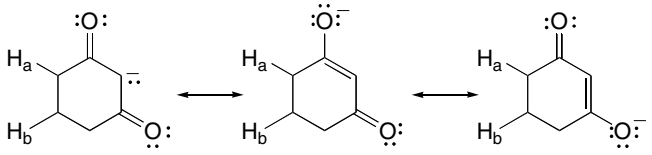
loss of H_a:



2 resonance structures

intermediate stability

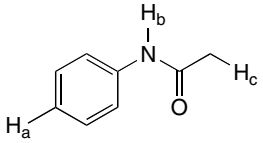
loss of H_c:



3 resonance structures

most stable conjugate base

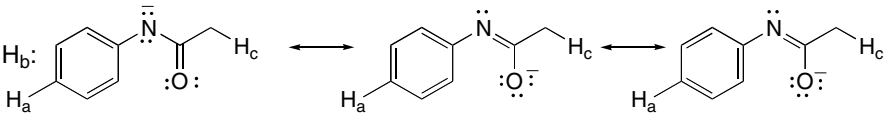
b.



acetanilide

increasing acidity: $H_a < H_c < H_b$

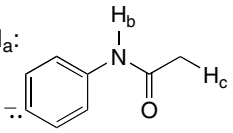
loss of H_b:



7 resonance structures

most stable conjugate base

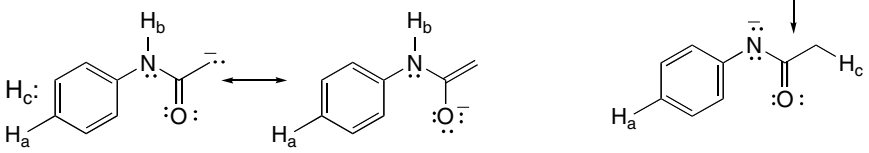
loss of H_a:



one Lewis structure

least stable conjugate base

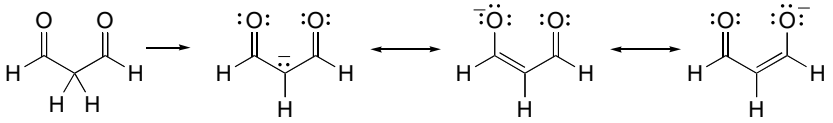
loss of H_c:



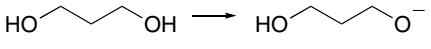
2 resonance structures that delocalize the negative charge

intermediate stability

19.49

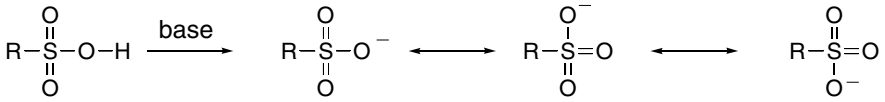


The conjugate base is resonance stabilized. Two of the structures place a negative charge on an O atom.
weaker conjugate base
stronger acid

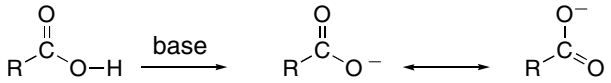


The conjugate base has only one Lewis structure.
stronger conjugate base
weaker acid

19.50 As usual, compare the stability of the conjugate bases. With RSO_3H, loss of a proton forms a conjugate base that has three resonance structures, all of which are equivalent and place a negative charge on a more electronegative O atom. With the conjugate base of RCOOH, there are only two of these resonance structures. Thus, the conjugate base RSO_3^- is more highly resonance stabilized than $RCOO^-$, so RSO_3H is a stronger acid than RCOOH.

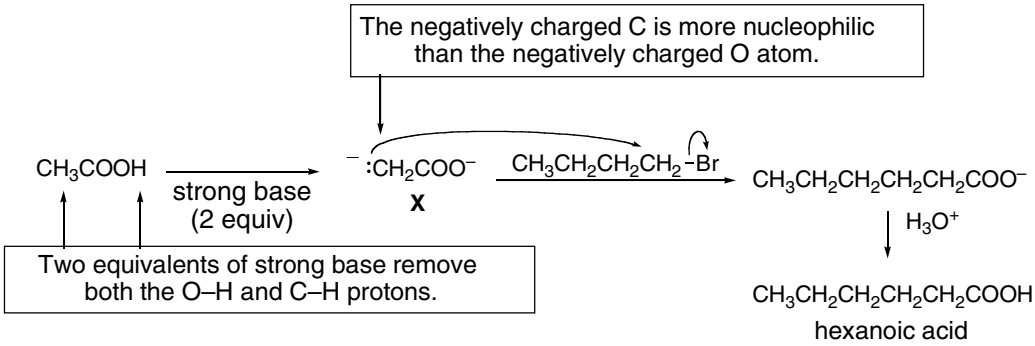


three resonance structures for the conjugate base

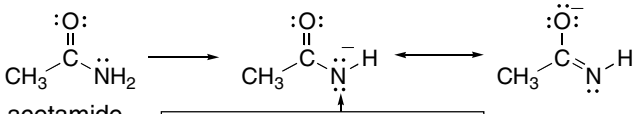


two resonance structures for the conjugate base

19.51



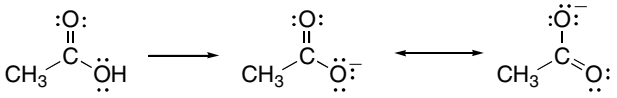
19.52



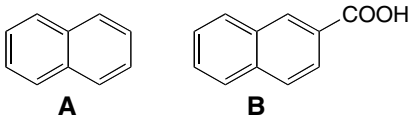
acetamide

somewhat less stable with the (–) charge on N

O is more electronegative than N, making the conjugate base of CH_3COOH more stable than the conjugate base of acetamide. Therefore, acetamide is less acidic.



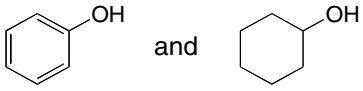
19.53



A **B**

- Dissolve both compounds in CH_2Cl_2.
- Add 10% $NaHCO_3$ solution. This makes a carboxylate anion ($C_{10}H_7COO^-$) from **B**, which dissolves in the aqueous layer. The other compound (**A**) remains in the CH_2Cl_2.
- Separate the layers.

19.54

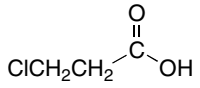


- Dissolve both compounds in CH_2Cl_2.
- Add 10% NaOH solution. This converts C_6H_5OH into a phenoxide anion, $C_6H_5O^-$, which dissolves in the aqueous solution. The alcohol remains in the organic layer (neutral) since it is not acidic enough to be deprotonated to any significant extent by NaOH.
- Separate the layers.

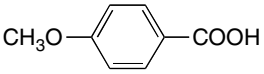
19.55 To separate two compounds in an aqueous extraction, one must be water soluble (or be able to be converted into a water-soluble ionic compound by an acid–base reaction), and the other insoluble. 1-Octanol has greater than 5 C's, making it insoluble in water. Octane is an alkane, also insoluble in water. Neither compound is acidic enough to be deprotonated by a base in aqueous solution. Since their solubility properties are similar, they cannot be separated by an extraction procedure.

19.56

a. Molecular formula: $C_3H_5ClO_2$ ⟶ one double bond or ring
IR: 3500–2500 cm^{-1}, 1714 cm^{-1} ⟶ C=O and O–H
NMR data: 2.87 (triplet, 2 H), 3.76 (triplet, 2 H), and 11.8 (singlet, 1 H) ppm

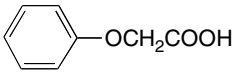


b. Molecular formula: $C_8H_8O_3$ ⟶ 5 double bonds or rings
IR: 3500–2500 cm^{-1}, 1688 cm^{-1} ⟶ C=O and O–H
NMR data: 3.8 (singlet, 3 H), 7.0 (doublet, 2 H), 7.9 (doublet, 2 H), and 12.7 (singlet, 1 H) ppm



para disubstituted benzene ring

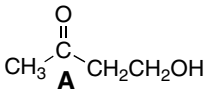
c. Molecular formula: $C_8H_8O_3$ ⟶ 5 double bonds or rings
IR: 3500–2500 cm^{-1}, 1710 cm^{-1} ⟶ C=O and O–H
NMR data: 4.7 (singlet, 2 H), 6.9–7.3 (multiplet, 5 H), and 11.3 (singlet, 1 H) ppm



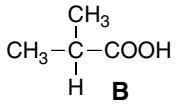
monosubstituted benzene ring

19.57

Compound **A**: Molecular formula $C_4H_8O_2$ (one degree of unsaturation)
IR absorptions at 3600–3200 (O–H), 3000–2800 (C–H), and 1700 (C=O) cm^{-1}
^1H NMR data:

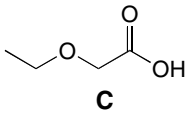
Absorption	ppm	# of H's	Explanation	Structure:
singlet	2.2	3	a CH_3 group	
singlet	2.55	1	1 H adjacent to none or OH	
triplet	2.7	2	2 H's adjacent to 2 H's	
triplet	3.9	2	2 H's adjacent to 2 H's	

Compound **B**: Molecular formula $C_4H_8O_2$ (one degree of unsaturation)
IR absorptions at 3500–2500 (O–H) and 1700 (C=O) cm^{-1}
^1H NMR data:

Absorption	ppm	# of H's	Explanation	Structure:
doublet	1.6	6	6 H's adjacent to 1 H	
septet	2.3	1	1 H adjacent to 6 H's	
singlet (very broad)	10.7	1	OH of RCOOH	

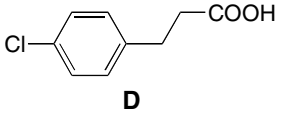
19.58

Compound **C**: Molecular formula $C_4H_8O_3$ (one degree of unsaturation)
IR absorptions at 3600–2500 (O–H) and 1734 (C=O) cm^{-1}
^1H NMR data:

Absorption	ppm	# of H's	Explanation	Structure:
triplet	1.2	3	a CH_3 group adjacent to 2 H's	
quartet	3.6	2	2 H's adjacent to 3 H's	
singlet	4.1	2	2 H's	
singlet	11.3	1	OH of COOH	

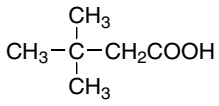
19.59

Compound **D**: Molecular formula $C_9H_9ClO_2$ (five degrees of unsaturation)
^{13}C NMR data: 30, 36, 128, 130, 133, 139, 179 = 7 different types of C's
^1H NMR data:

Absorption	ppm	# of H's	Explanation	Structure:
triplet	2.7	2	2 H's adjacent to 2 H's	
triplet	2.9	2	2 H's adjacent to 2 H's	
two signals	7.2	4	on benzene ring	
singlet	11.7	1	OH of COOH	

19.60

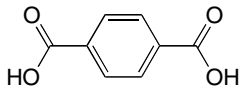
Molecular formula $C_6H_{12}O_2$ (1 double bond due to COOH)
^1H NMR: 1.1 (singlet), 2.2 (singlet), and 11.9 (singlet) ppm



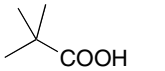
19.61

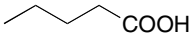
Molecular formula: $C_8H_6O_4$: 6 degrees of unsaturation
IR 1692 cm^{-1} (C=O)
^1H NMR 8.2 and 10.0 ppm (singlets)

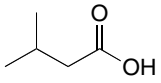
aromatic H COOH



19.62

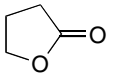
A 
3 different C's
Spectrum [2]: peaks at 27, 39, 186 ppm

B 
5 different C's
Spectrum [1]: peaks at 14, 22, 27, 34, 181 ppm

C 
4 different C's
Spectrum [3]: peaks at 22, 26, 43, 180 ppm

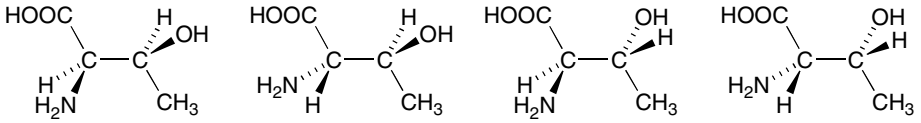
19.63

GBL: Molecular formula $C_4H_6O_2$ (two degrees of unsaturation)
IR absorption at 1770 (C=O) cm^{-1}
^1H NMR data:

Absorption	ppm	# of H's	Explanation	Structure:
multiplet	2.28	2	2 H's adjacent to several H's	
triplet	2.48	2	2 H's adjacent to 2 H's	**GBL**
triplet	4.35	2	2 H's adjacent to 2 H's	

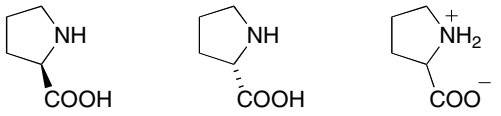
19.64

threonine



2R,3*S* *2S*,3*S* *2R*,3*R* *2S*,3*R*
naturally occurring

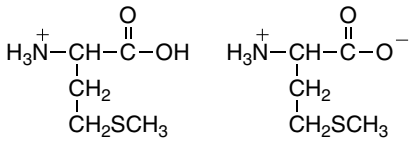
19.65



proline enantiomer zwitterion

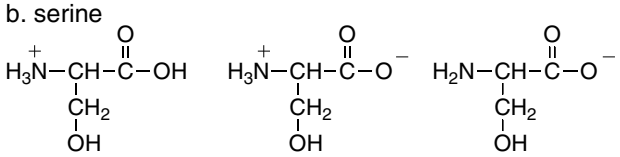
19.66

a. methionine



pH = 1 pH = 6 form at isoelectric point pH = 11

b. serine



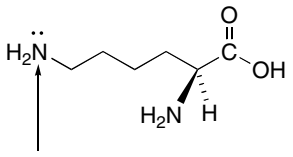
pH = 1 pH = 6 form at isoelectric point pH = 11

19.67

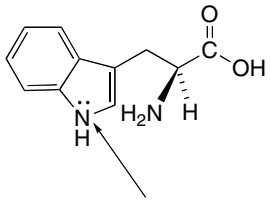
a. cysteine $pI = \dfrac{pK_a(COOH) + pK_a(NH_3^+)}{2} = (2.05) + (10.25) / 2 = \mathbf{6.15}$

b. methionine $pI = \dfrac{pK_a(COOH) + pK_a(NH_3^+)}{2} = (2.28) + (9.21) / 2 = \mathbf{5.75}$

19.68

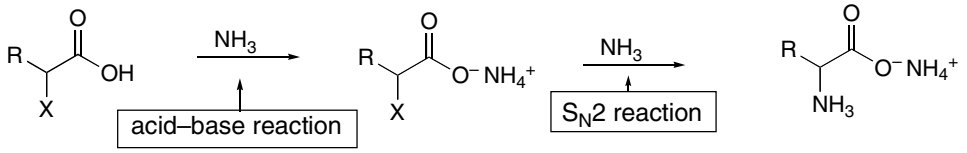


lysine
This lone pair is localized on the N atom, making it a base.



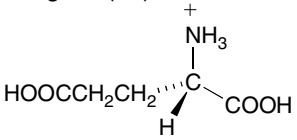
tryptophan
This lone pair is delocalized in the π system to give 10 π electrons, making it aromatic. This is similar to pyrrole (Chapter 17). Since these electrons are delocalized in the aromatic system, this N atom in tryptophan is not basic.

19.69 The first equivalent of NH_3 acts as a base to remove a proton from the carboxylic acid. A second equivalent then acts as a nucleophile to displace X to form the ammonium salt of the amino acid.

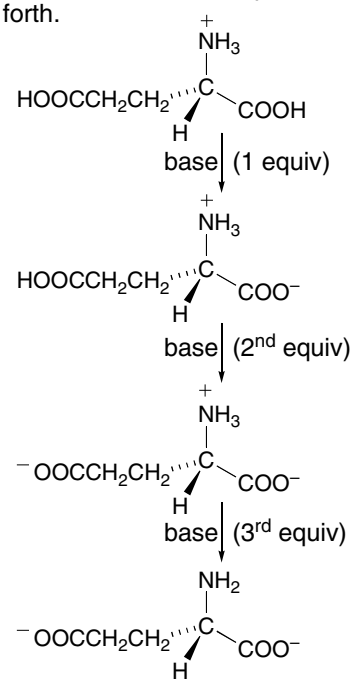


19.70

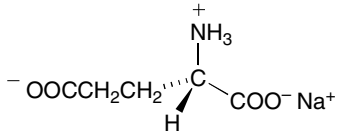
a. At pH = 1, the net charge is (+1).



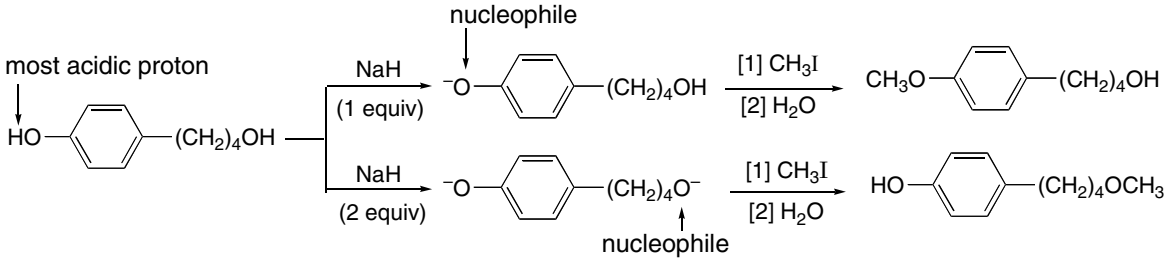
b. increasing pH: As base is added, the most acidic proton is removed first, then the next most acidic proton, and so forth.



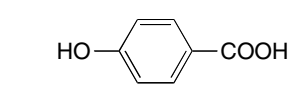
c. monosodium glutamate



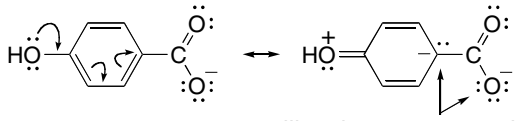
19.71 The first equivalent of NaH removes the most acidic proton; that is, the OH proton on the phenol. The resulting phenoxide can then act as a nucleophile to displace I to form a substitution product. With two equivalents, both OH protons are removed. In this case the more nucleophilic O atom is the stronger base; that is, the alkoxide derived from the alcohol (not the phenoxide), so this negatively charged O atom reacts first in a nucleophilic substitution reaction.



19.72

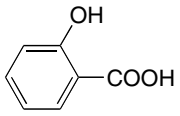


p-hydroxybenzoic acid
less acidic than benzoic acid

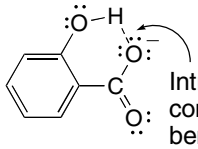


like charges on nearby atoms
destabilizing

The OH group donates electron density by its resonance effect and this destabilizes the conjugate base, making the acid less acidic than benzoic acid.

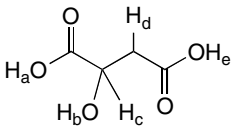


o-hydroxybenzoic acid
more acidic than benzoic acid



Intramolecular hydrogen bonding stabilizes the conjugate base, making the acid more acidic than benzoic acid.

19.73



2-hydroxybutanedioic acid
increasing acidity:
$H_d < H_c < H_b < H_e < H_a$

H_a and H_e must be the two most acidic protons since they are part of carboxylic acids. Loss of a proton forms a resonance-stabilized carboxylate anion that has the negative charge delocalized on two O atoms. H_a is more acidic than H_e because the nearby OH group on the α carbon increases acidity by an electron-withdrawing inductive effect. H_b is the next most acidic proton because the conjugate base places a negative charge on the electronegative O atom, but it is not resonance stabilized.

The least acidic H's are H_c and H_d since these H's are bonded to C atoms. The electronegative O atom further acidifies H_c by an electron-withdrawing inductive effect.