

Chapter 18: Carboxylic Acids

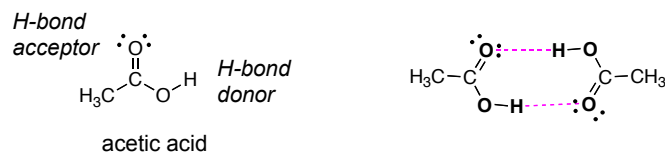
18.1: Carboxylic Acid Nomenclature (please read)

suffix: -oic acid

18.2: Structure and Bonding (please read)

18.3: Physical Properties. The carboxylic acid functional group contains both a hydrogen bond donor (-OH) and a hydrogen bond acceptor (C=O).

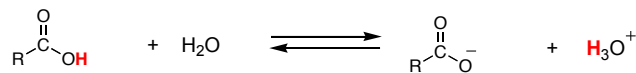
Carboxylic acids exist as hydrogen bonded dimers.



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18.4: Acidity of Carboxylic Acids. The pK_a of carboxylic acids typically ~ 5 . They are significantly more acidic than water or alcohols.

Bronsted Acidity (Ch. 1.13): Carboxylic acids transfer a proton to water to give H_3O^+ and carboxylate anions, RCO_2^-



$$K_a = \frac{[RCO_2^-][H_3O^+]}{[RCO_2H]}$$

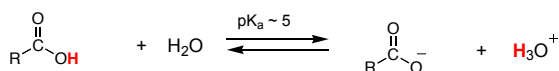
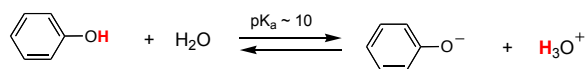
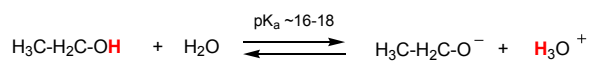
$$pK_a = -\log K_a$$

typically $\sim 10^{-5}$
for carboxylic acid

typically ~ 5 for
carboxylic acid

pK_a	CH_3CH_3 $\sim 50-60$	CH_3CH_2OH 16	$PhOH$ 10	CH_3CO_2H 4.7	HCl -7
	$\xrightarrow{\text{Increasing acidity}} \xrightarrow{\hspace{10em}}$				

$\xrightarrow{\text{Increasing acidity}} \xrightarrow{\hspace{10em}}$ 145

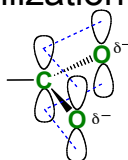


The greater acidity of carboxylic acids is attributed to greater stabilization of carboxylate ion by:

a. Inductive effect of the $C=O$ group



b. Resonance stabilization of the carboxylate ion



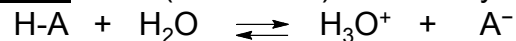
4 π -electrons delocalized
over three p-orbitals

C-O bond length of a
carboxylate are the same

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Bronsted Acid: proton donor (H^+)

weak acids (and bases) do not fully dissociate



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H-A}]} \quad \text{acid dissociation constant}$$

$$\text{p}K_a = -\log K_a$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

Henderson-Hasselbalch Equation: Relates $\text{p}K_a$ with pH

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{H-A}]}$$

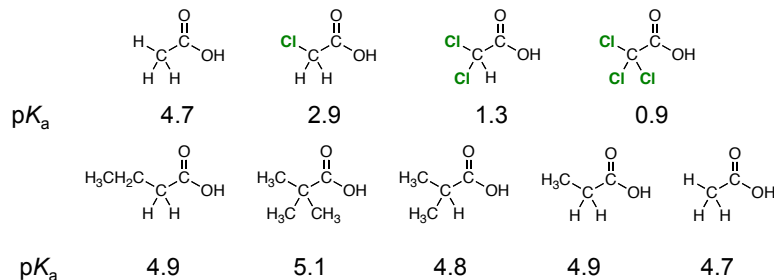
when $[\text{A}^-] = [\text{H-A}]$, the $\text{pH} = \text{p}K_a$

$$\text{pH} - \text{p}K_a = \log \frac{[\text{A}^-]}{[\text{H-A}]}$$

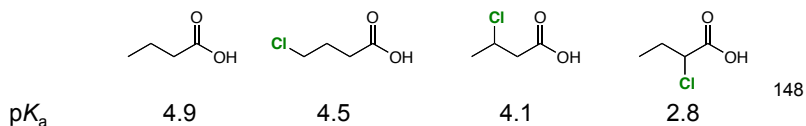
$$\frac{[\text{A}^-]}{[\text{H-A}]} = 10^{(\text{pH} - \text{p}K_a)}$$

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
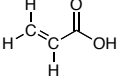
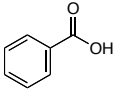
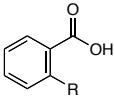
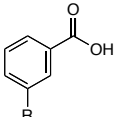
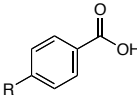
18.5: Substituents and Acid Strength. The $\text{p}K_a$ of a carboxylic acid can be influenced by substituents on the α -carbon, largely through inductive effects. Electron-withdrawing groups increase the acidity (lower $\text{p}K_a$) and electron-donating groups decrease the acidity (higher $\text{p}K_a$). (see table 18.2, p. 743)



Inductive effects work through σ -bonds, and the effect falls off dramatically with distance

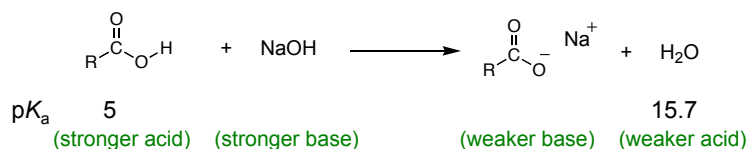


18.6: Ionization of Substituted Benzoic Acids. The charge of the carboxylate ion cannot be delocalize into the aromatic ring. Electron-donating groups decrease the acidity. Electron-withdrawing groups increase the acidity. (Table 18.3, p. 745)

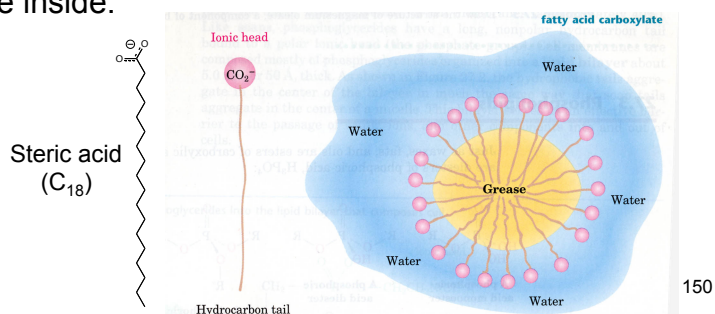
				
pK_a		4.7	4.3	4.2
				
R=	pK_a			
-CH ₃		3.9	4.3	4.4
-F		3.3	3.9	4.1
-Cl		2.9	3.8	4.0
-Br		2.8	3.8	4.0
-OCH ₃		4.1	4.1	4.5
-NO ₂		2.2	3.5	3.4

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18.7: Salts of Carboxylic Acids. Carboxylic acids react with base to give carboxylate salts.

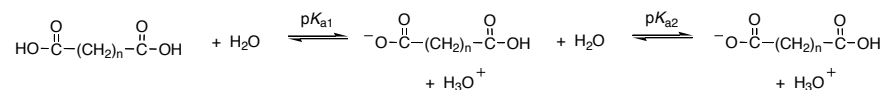


Detergents and Micelles: substances with polar (*hydrophilic*) head groups and *hydrophobic* tail groups form aggregates in water with the carboxylate groups on the outside and nonpolar tails on the inside.



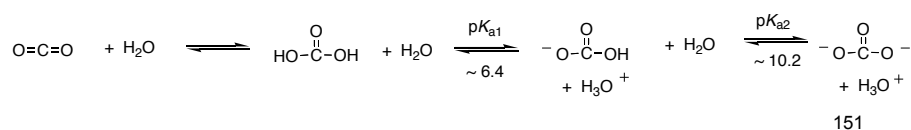
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18.8: Dicarboxylic Acids. one carboxyl group acts as an electron-withdrawing group toward the other and lowers its pKa; the effect decreases with increasing separation



Oxalic acid (n= 0)	pK _{a1} = 1.2	pK _{a2} = 4.2
Malonic acid (n= 1)	2.8	5.7
Succinic acid (n=2)	4.2	5.6
Glutaric acid (n=3)	4.3	5.7
Adipic acid (n=4)	4.4	5.4
Pimelic acid (n=5)	4.7	5.6

18.9: Carbonic Acid (please read)



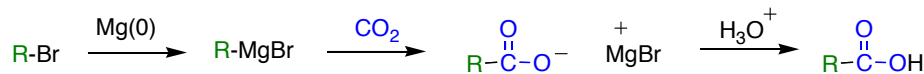
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18.10: Sources of Carboxylic Acids. Summary of reaction from previous chapters that yield carboxylic acids (Table 18.4, p. 791)

- Side-chain oxidation of alkylbenzene to give benzoic acid derivatives (Ch. 11.12): reagent: K₂Cr₂O₇, H₃O⁺ -or- KMnO₄
- Oxidation of primary alcohols (Ch. 15.9)
reagent: K₂Cr₂O₇, H₃O⁺
- Oxidation of aldehydes (Ch. 17.14)
reagent: K₂Cr₂O₇, H₃O⁺

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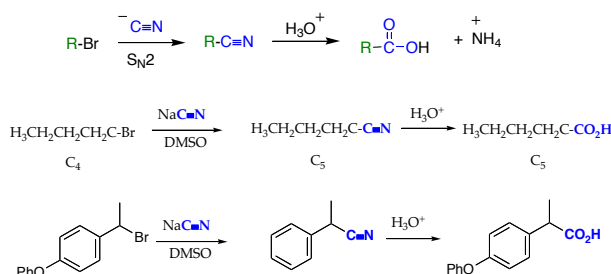
18.11: Synthesis of Carboxylic Acids by the Carboxylation of Grignard Reagents. Grignard reagents react with CO_2 to afford carboxylic acids. An additional carbon (the CO_2H group, which is derived from CO_2) is added to the Grignard reagent.



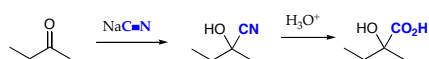
Grignard reagents are strong bases and strong nucleophiles. As such, they are incompatible with acidic (alcohols, thiols, amines, carboxylic acid, amides,) or electrophilic (aldehydes, ketones, esters, nitrile, halides) groups.

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18.12: Synthesis of Carboxylic Acids by the Preparation and Hydrolysis of Nitriles. Cyanide ion is an excellent nucleophile and will react with 1° and 2° alkyl halides and tosylates to give nitriles. This reaction adds one carbon. The nitrile can be hydrolyzed to a carboxylic acid



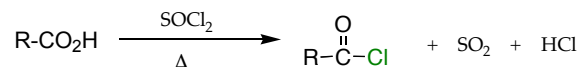
Cyanohydrins (Ch. 17.7) are hydrolyzed to α -hydroxy-carboxylic acids.



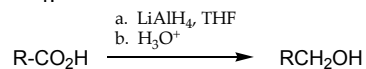
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18.13: Reactions of Carboxylic Acids: A Review and Preview.
(Table 18.5, p. 753)

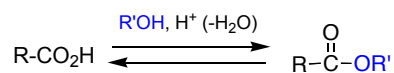
a. Conversion to acid chlorides (Ch. 12.7). Reagent: SOCl_2



b. Reduction to a 1° alcohol (Ch. 15.3). Reagent: LiAlH_4
Carboxylic acids are reduced to 1° alcohols by LAH,
but not by NaBH_4 .

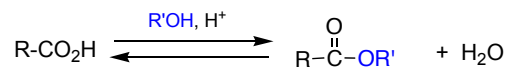


c. Acid-catalyzed esterification (Ch. 15.8)
Reagent: alcohol ($\text{R}'\text{OH}$), H^+ ($-\text{H}_2\text{O}$)



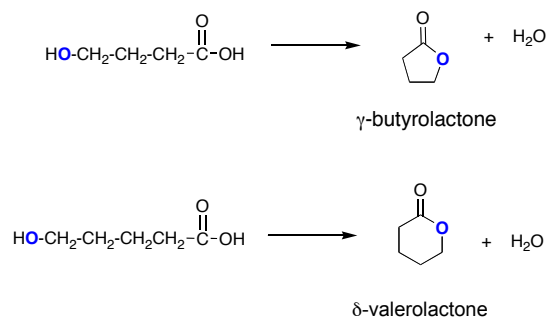
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18.14: Mechanism of Acid-Catalyzed Esterification.
Fischer Esterification (p. 754-755)



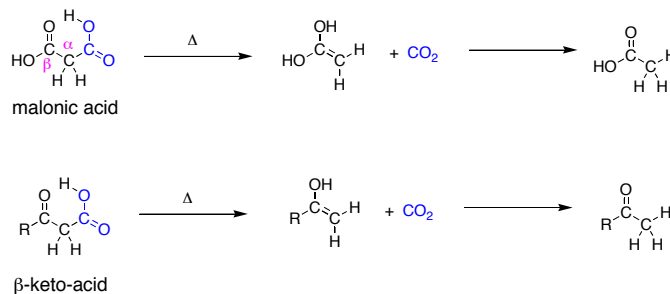
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18.15: Intramolecular Ester Formation: Lactones. Lactones are cyclic esters derived from the intramolecular esterification of hydroxy-carboxylic acids. 4-Hydroxy and 5-hydroxy acids cyclize readily to form 5- and 6-membered ring (γ and δ) lactones.



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18.16: Decarboxylation of Malonic Acid and Related Compounds. Carboxylic acids with a carbonyl or nitrile group at the β -position will decarboxylate (lose CO_2) upon heating



Decarboxylation initially leads to an enol of the β -carbonyl group. This is a key step in the *acetoacetic ester synthesis* and *malonic acid synthesis* (Ch. 20.6).

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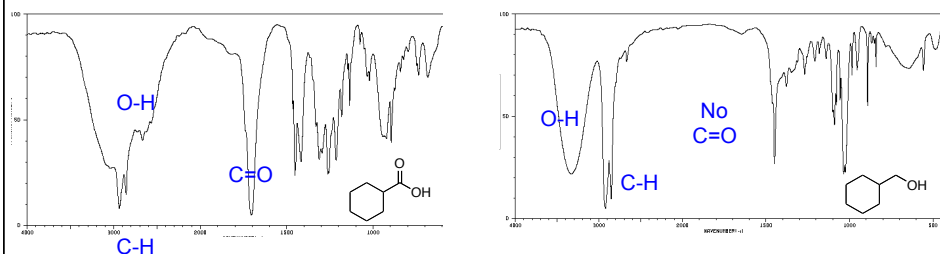
18.17: Spectroscopic Analysis of Carboxylic Acids

Infrared Spectroscopy

Carboxylic acids:

Very broad O-H absorption between $2500 - 3300 \text{ cm}^{-1}$
broader than that of an alcohol

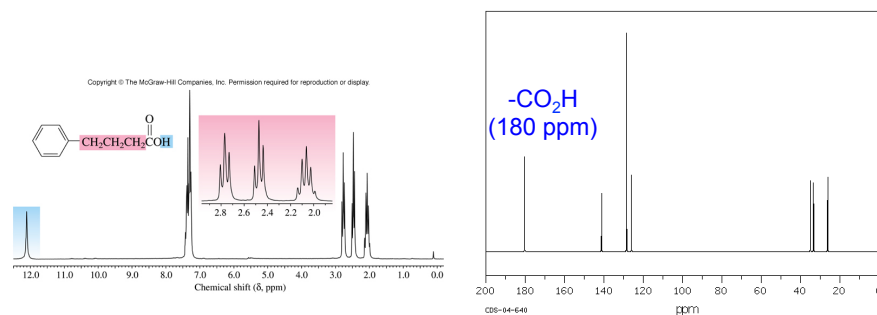
Strong C=O absorption bond between $1700 - 1730 \text{ cm}^{-1}$



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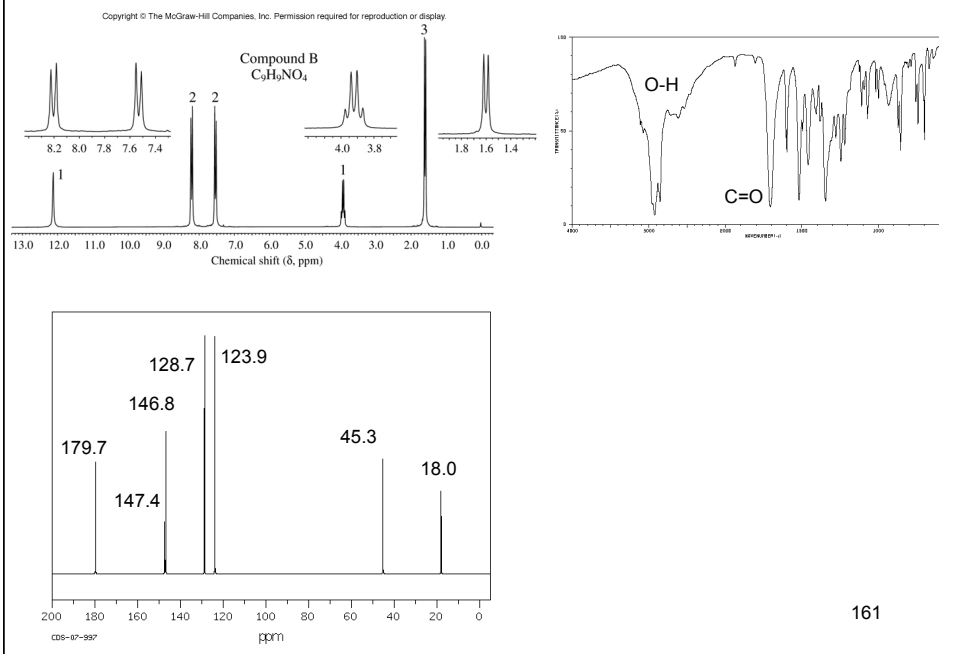
$^1\text{H NMR}$: The $-\text{CO}_2\text{H}$ proton is a broad singlet near $\delta \sim 12$. When D_2O is added to the sample the $-\text{CO}_2\text{H}$ proton is replaced by D causing the resonance to disappear (same for alcohols). The $-\text{CO}_2\text{H}$ proton is often not observed.

$^{13}\text{C NMR}$: The chemical shift of the carbonyl carbon in the ^{13}C spectrum is in the range of $\sim 165 - 185$. This range is distinct from the aldehyde and ketone range ($\sim 190 - 220$)



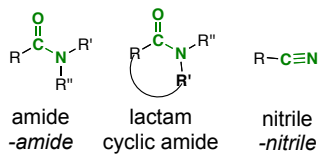
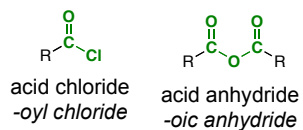
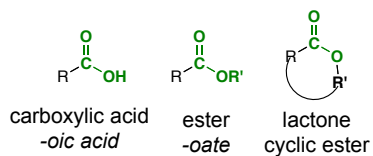
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problem 18.33b



Chapter 19: Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution

19.1: Nomenclature of Carboxylic Acid Derivatives (please read)



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