

The Chemistry of Carboxylic Acids

April 15, 2013

- Spectroscopy.
- Acidity.
- Synthesis of carboxylic acids (review).
- Acid-catalyzed esterification.

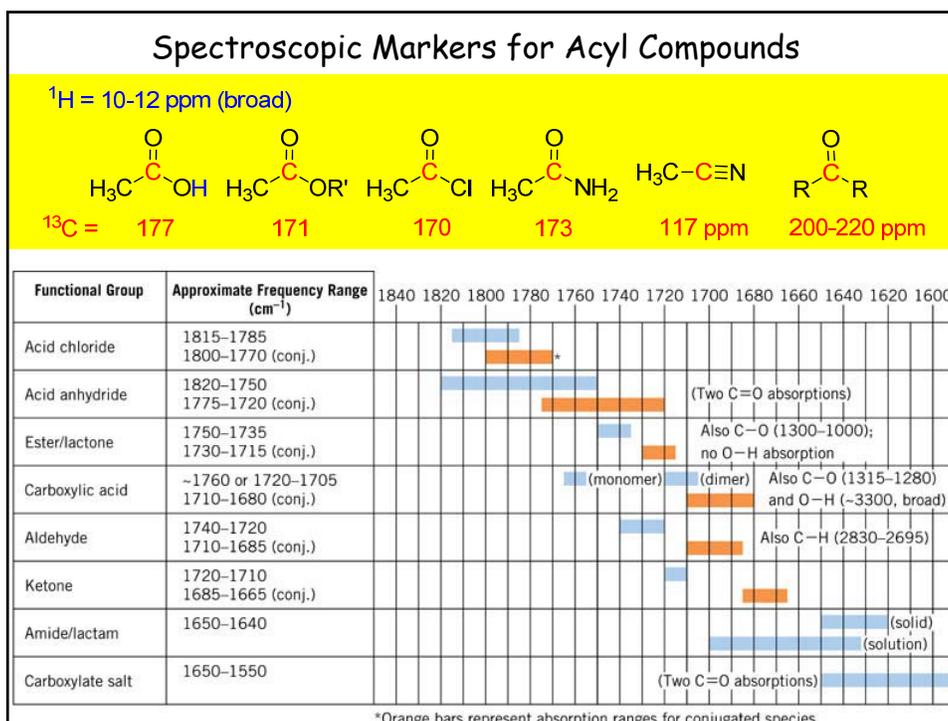
Announcements

Suggested Problems for Chapter 20: 20.25, 20.27, 20.30, 20.32, 20.35, 20.38, 20.40, 20.43, 20.45, 20.46, 20.49, 20.51, 20.53, 20.55.

TA Office Hours: Mon 7-8 pm: Rob Craig - 302 Schlinger (x4056); Tue 3-4 pm: Kelly Kim - 302 Schlinger (x4047); Tue 7-8 pm: Corey Reeves - 302 Schlinger (x4056); Wed 5-6 pm: Adam Boynton - 139 Noyes (x3202); Wed 8-9 pm: Ben Suslick (UTA) - Lloyd Lounge; Thu 8-9 pm: Evan Zhao (UTA) - Fleming Lounge; Thu 9-10 pm: Crystal Chu - 202 Schlinger (x3634); Sun 3-4 pm: Chung Wan Lee - 302 Schlinger (x4056)

Carboxylic and Dicarboxylic Acids

Structure	Systematic	Common	mp (°C)	bp (°C)	H ₂ O sol (g/100ml)	pK ₁	pK ₂
HCOOH	methanoic	formic			∞	3.75	
CH ₃ COOH	ethanoic	acetic	16.6	118	∞	4.76	
CH ₃ CH ₂ COOH	propanoic	propionic			∞	4.87	
CH ₃ CH ₂ CH ₂ COOH	butanoic	butyric			∞	4.81	
CH ₃ (CH ₂) ₃ COOH	pentanoic	valeric			5	4.82	
CH ₃ (CH ₂) ₄ COOH	hexanoic	caproic			1	4.84	
CH ₃ (CH ₂) ₁₀ COOH	dodecanoic	lauric			0.006	5.3	
CH ₃ (CH ₂) ₁₄ COOH	hexadecanoic	palmitic			.002	6.46	
CH ₃ (CH ₂) ₁₆ COOH	octadecanoic	stearic			.0003	-	
Ph-COOH	benzoic	benzoic			0.34	4.19	
HO ₂ CCO ₂ H		oxalic				1.2	4.2
HO ₂ CCH ₂ CO ₂ H		malonic				2.9	5.7
HO ₂ C(CH ₂) ₂ CO ₂ H		succinic				4.2	5.6
HO ₂ C(CH ₂) ₃ CO ₂ H		glutaric				4.3	5.4
HO ₂ C(CH ₂) ₄ CO ₂ H		adipic				4.4	5.6
HOOC  COOH		maleic				1.9	6.1
HOOC  COOH		fumaric				3.0	4.4



Thermodynamic Considerations for Acidity

$$\text{X}-\text{C}(\text{Y})(\text{Z})-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{X}-\text{C}(\text{Y})(\text{Z})-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- + \text{H}_3\text{O}^+$$

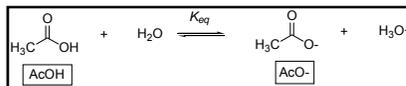
Acid	pK_a	ΔG°	ΔH°	$-\text{T}\Delta S^\circ$
CH_3COOH	4.76	+6.5	-0.1	+6.6
ClCH_2COOH	2.86	+3.9	-1.1	+5.0

Recall: $\Delta G^\circ = \Delta H^\circ - \text{T}\Delta S^\circ$

ΔG , ΔH , and $\text{T}\Delta S$ are in kcal/mol.

The Henderson-Hasselbalch Equation: A Review

Consider the partial ionization of acetic acid:



The equilibrium constant is defined as:

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{AcO}^-]}{[\text{H}_2\text{O}][\text{AcOH}]}$$

The acid dissociation constant, K_a , is obtained by rearranging terms:

$$K_a = K_{eq}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{AcO}^-]}{[\text{AcOH}]}$$

Take the $-\log$ of both sides,

$$-\log K_a = -\log \frac{[\text{H}_3\text{O}^+][\text{AcO}^-]}{[\text{AcOH}]}$$

and separate terms:

$$-\log K_a = -\log[\text{H}_3\text{O}^+] - \log \frac{[\text{AcO}^-]}{[\text{AcOH}]}$$

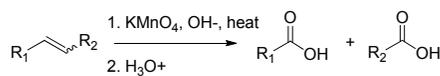
Now define $pK_a = -\log K_a$ and $pH = -\log [\text{H}_3\text{O}^+]$. Substitution yields: $pK_a = pH - \log \frac{[\text{AcO}^-]}{[\text{AcOH}]}$

or

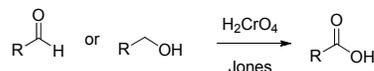
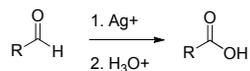
$$pH = pK_a + \log \frac{[\text{AcO}^-]}{[\text{AcOH}]}$$

an expression usually referred to as the Henderson-Hasselbalch equation.

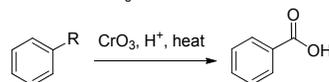
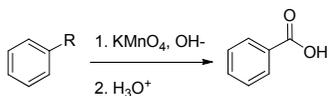
1. Oxidation of alkenes:



2. Oxidation of aldehydes & primary alcohols:

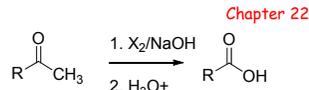


3. Oxidation of alkylbenzenes:

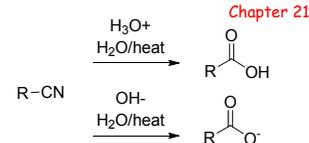


R = Me, primary, secondary alkyl.

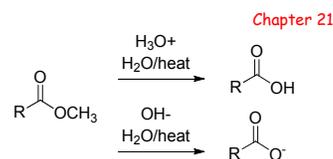
4. Oxidation of methyl ketones:



5. Hydrolysis of nitriles:



6. Hydrolysis of esters:



7. Carbonation of a Grignard:

