

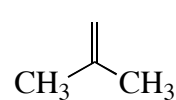
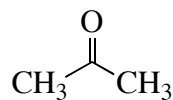
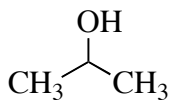
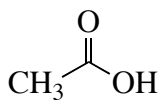
Lecture Notes  
Chem 51C  
S. King

Chapter 19 Carboxylic Acids & the Acidity of the O-H Bond

Carboxylic acids contain the carboxy group:

**I. Structure and Physical Properties of Carboxylic Acids:**

Compare physical properties:



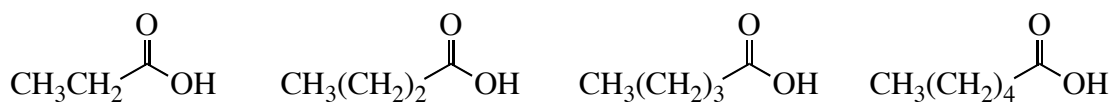
B.P.

%sol. in  
H<sub>2</sub>O

Q. Why do carboxylic acids have such high boiling points relative to many other organic compounds about the same molecular mass and shape?

A.

As the length of the carbon chain increases, the boiling points of a homologous series of carboxylic acids also increases, and the water solubility decreases:



B.P.

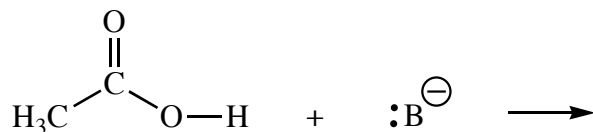
%sol. in  
H<sub>2</sub>O

**Why??**

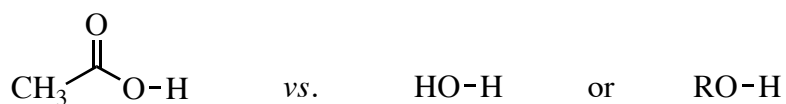
## II. Nomenclature (*see handout*)

## III. Acidity of Carboxylic Acids

When a carboxylic acid is treated with base, the proton on the carboxylate oxygen is abstracted to produce a carboxylate anion.



- The carbonyl adjacent to the hydroxyl group enhances the acidity of these protons.



Q. Why are carboxylic acids more acidic than alcohols or H<sub>2</sub>O?

A. 2 reasons:

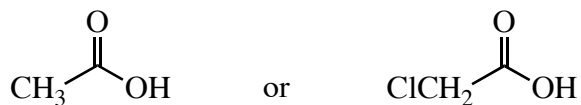
- Look at the conjugate bases:

2. The carbonyl group draws e-s away from the OH group which increases the  $\delta^+$  of the H atom and stabilizes the carboxylate.

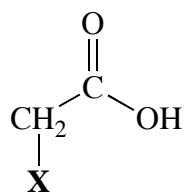
Substituents affect the acidity of carboxylic acids:

- *Anything that stabilizes the negatively charged conjugate base, makes the corresponding acid more acidic.*

**Example 1:** Which compound is more acidic?

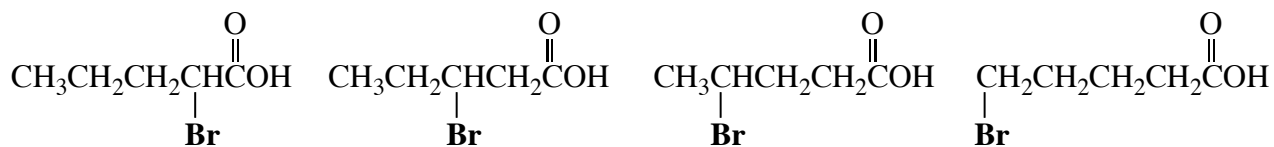


Look at effect of other substituents on Acetic Acid Derivatives:

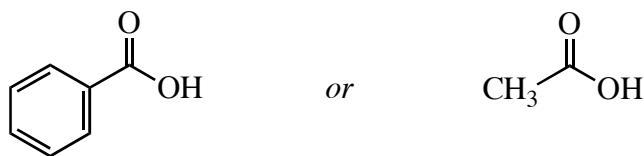


X	pK <sub>a</sub>	Electronegativity
H	4.76	2.1
I	3.17	2.4
Br	2.90	2.8
Cl	2.86	3.0
F	2.59	4.0
<hr/>		
OH	3.83	
CN	2.46	
NO <sub>2</sub>	1.68	
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CH <sub>3</sub>	4.87	

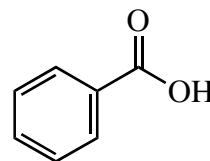
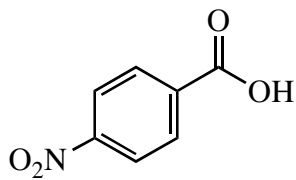
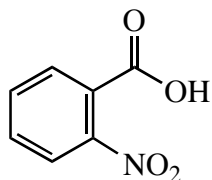
*Inductive effect decreases as the e<sup>-</sup> withdrawing group gets further away:*



**Example 2:** Which compound is more acidic?



**Example 3:** Which compound is more acidic?



**Common bases used to deprotonate carboxylic acids:**

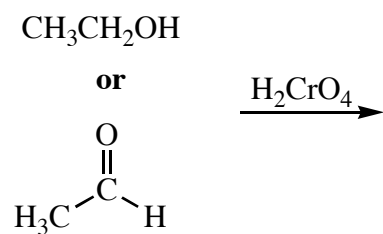
An acid can be deprotonated by a base that has a conjugate acid with a higher pKa. Since the pKa's of many carboxylic acids are  $\approx 5$ , bases that have conjugate acids with pKa values higher than 5 are strong enough to deprotonate them.

SOME TYPICAL BASES:	CONJUGATE ACID (pK <sub>A</sub> )
HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub> (6.4)
NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup> (9.4)
CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup> (10.2)
HO <sup>-</sup>	H <sub>2</sub> O (15.7)
RO <sup>-</sup> (CH <sub>3</sub> O <sup>-</sup> , EtO <sup>-</sup> )	ROH (16)
H <sup>-</sup>	H <sub>2</sub> (35)

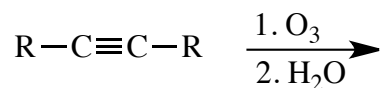
Example:

## IV. Preparation of Carboxylic Acids

### A. Oxidation of Aldehydes and 1° Alcohols

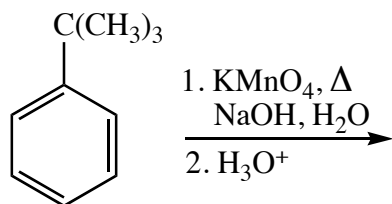
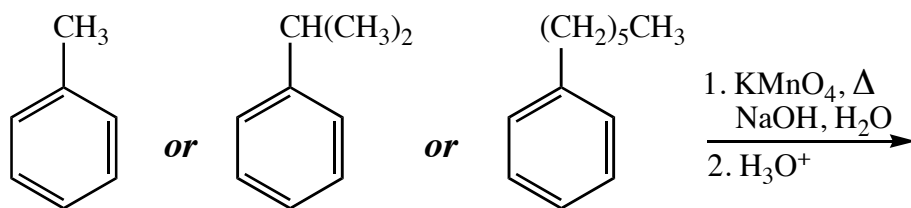


### B. Oxidative Cleavage of Alkenes & Alkynes: Ozonolysis

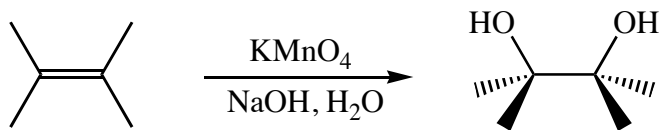


### C. Oxidation of Alkyl Groups Bonded to Aromatic Rings

An alkyl group bonded to a benzene ring can be oxidized to a carboxylic acid. Commonly used oxidizing agents are  $\text{KMnO}_4$  or  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_3\text{O}^+$ .



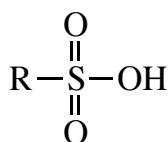
compare with:



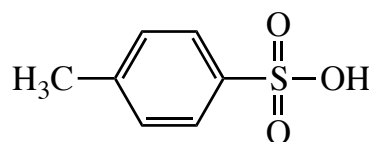
### III. Sulfonic Acids

Sulfonic acids have similar properties to carboxylic acids.

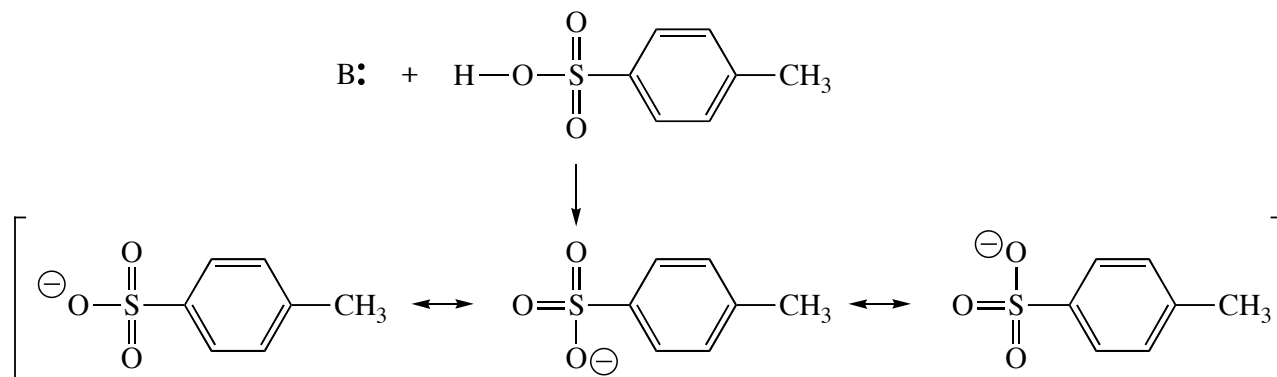
General Structure:



Example:



They are very strong acids ( $\text{pK}_a = -7!$ ) because their conjugate bases, sulfonate anions, are highly resonance stabilized.



Because their conjugate bases anions are such weak bases, they make great leaving groups.

