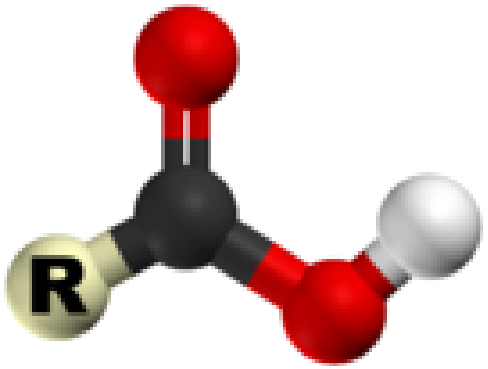
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 5-2

Carboxylic and Derivatives - Acidity



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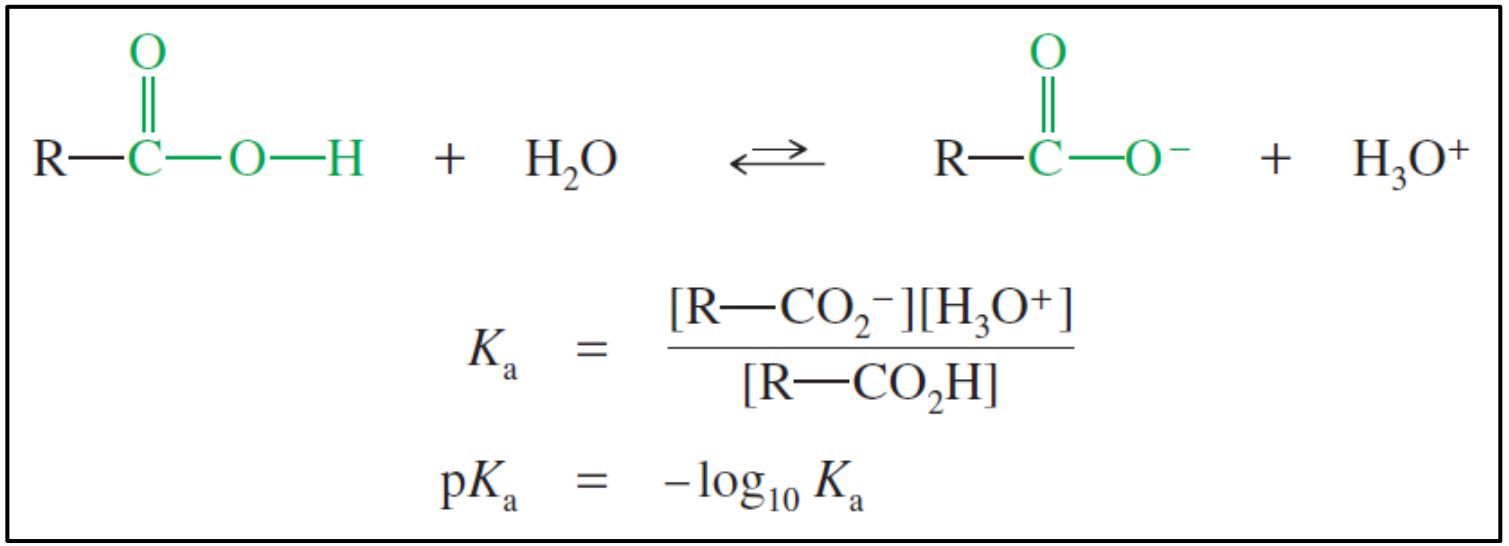
Recommended Textbook:

Chapter 20 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Acidities

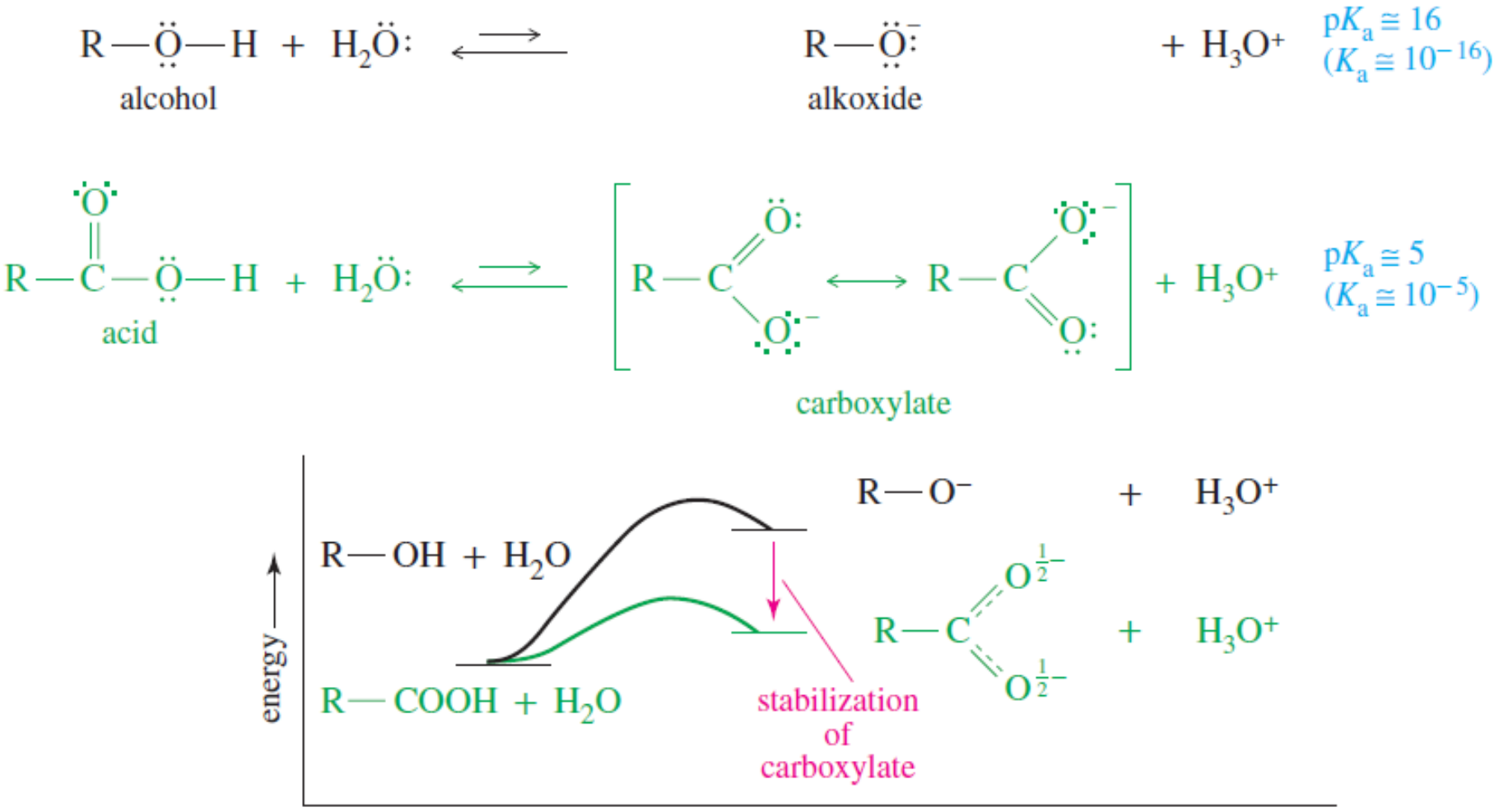
- A carboxylic acid may dissociate in water to give a **proton** and a **carboxylate ion**



- The equilibrium constant **K_a** is called the ***acid-dissociation constant***
- The **pK_a** of an acid is the **negative logarithm** of **K_a** and we commonly use as an **indication of the relative acidities** of different acids
- **Lower pK_a value = Stronger acid**

Acidities

- **Carboxylic acids** ($pK_a \sim 5$) are 10^{11} times more acidic than **alcohols** ($pK_a \sim 16$)



- Dissociation of a carboxylic acid gives a **carboxylate ion** with the negative charge **spread out equally over two oxygen atoms**, compared with just one oxygen in an alkoxide ion

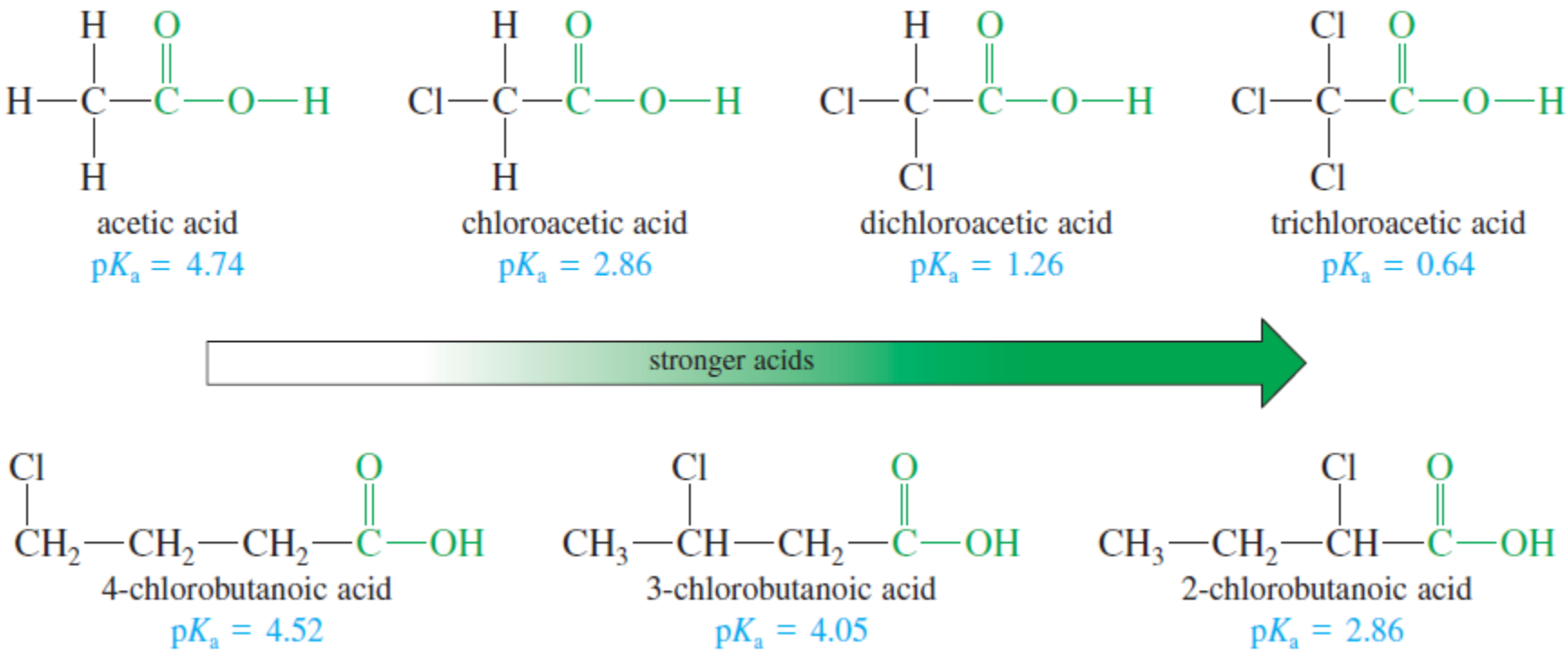
Acidities

TABLE 20-3 Values of K_a and pK_a for Carboxylic Acids and Dicarboxylic Acids

Formula	Name		
		Simple carboxylic acids	
		K_a (at 25 °C)	pK_a
HCOOH	formic acid	1.77×10^{-4}	3.75
CH_3COOH	acetic acid	1.76×10^{-5}	4.74
$CH_3CH_2\ COOH$	propionic acid	1.34×10^{-5}	4.87
$CH_3(CH_2)_2COOH$	butyric acid	1.54×10^{-5}	4.82
$CH_3(CH_2)_3COOH$	pentanoic acid	1.52×10^{-5}	4.81
$CH_3(CH_2)_4COOH$	hexanoic acid	1.31×10^{-5}	4.88
$CH_3(CH_2)_6COOH$	octanoic acid	1.28×10^{-5}	4.89
$CH_3(CH_2)_8COOH$	decanoic acid	1.43×10^{-5}	4.84
$C_6H_5\,COOH$	benzoic acid	6.46×10^{-5}	4.19
p-$CH_3C_6H_4COOH$	*p*-toluic acid	4.33×10^{-5}	4.36
p-ClC_6H_4COOH	*p*-chlorobenzoic acid	1.04×10^{-4}	3.98
p-$NO_2C_6H_4COOH$	*p*-nitrobenzoic acid	3.93×10^{-4}	3.41

Acidities – Substituent Effects

- Any substituent that **stabilises the negatively charged** carboxylate ion (i.e. **electron withdrawing**) promotes dissociation and results in a **stronger acid**



- The **magnitude** of a substituent effect depends on its **distance** from the carboxyl group

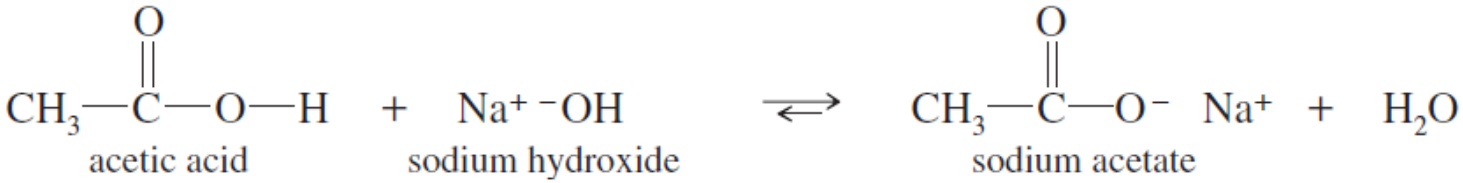
Acidities – Substituent Effects

TABLE 20-4 Values of K_a and pK_a for Substituted Carboxylic Acids

Acid	K_a	pK_a	
F_3CCOOH	5.9×10^{-1}	0.23	stronger acids
Cl_3CCOOH	2.3×10^{-1}	0.64	
$Cl_2CHCOOH$	5.5×10^{-2}	1.26	
$O_2N—CH_2COOH$	2.1×10^{-2}	1.68	
$NCCH_2COOH$	3.4×10^{-3}	2.46	
FCH_2COOH	2.6×10^{-3}	2.59	
$ClCH_2COOH$	1.4×10^{-3}	2.86	
$CH_3CH_2CHClCOOH$	1.4×10^{-3}	2.86	
$BrCH_2COOH$	1.3×10^{-3}	2.90	
ICH_2COOH	6.7×10^{-4}	3.18	
CH_3OCH_2COOH	2.9×10^{-4}	3.54	
$HOCH_2COOH$	1.5×10^{-4}	3.83	
$CH_3CHClCH_2COOH$	8.9×10^{-5}	4.05	
$PhCOOH$	6.46×10^{-5}	4.19	
$PhCH_2COOH$	4.9×10^{-5}	4.31	
$ClCH_2CH_2CH_2COOH$	3.0×10^{-5}	4.52	
CH_3COOH	1.8×10^{-5}	4.74	
$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82	

Salts of Carboxylic Acids

- A **strong base** can completely deprotonate a carboxylic acid. The products are a **carboxylate ion**, **the cation** remaining from the base, and **water**. The **combination of a carboxylate ion and a cation is a salt of a carboxylic acid**



Liquid / Solids with pungent smell

High melting point

Relatively soluble in water

Solids with little odour;

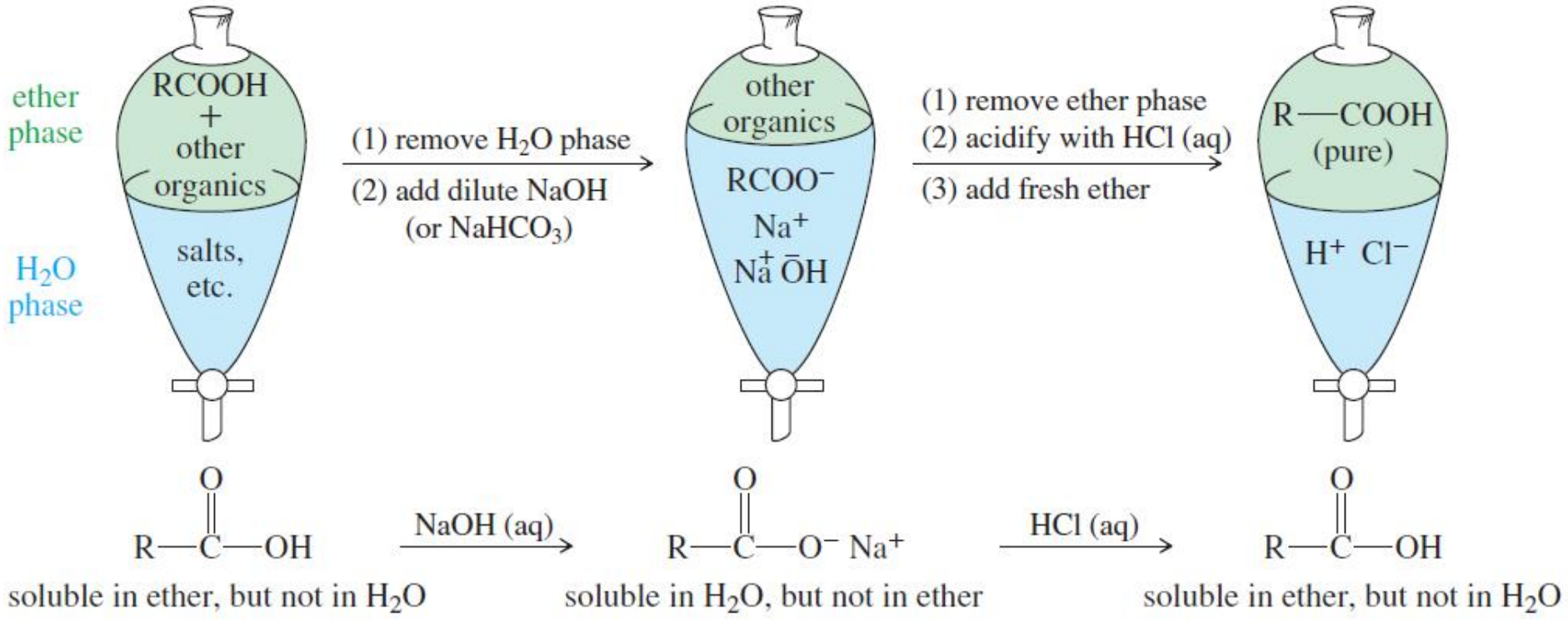
Very high melting point

Very soluble in water

- Addition of a **mineral acid** (more acidic) converts a carboxylic acid salt back to the original carboxylic acid

Acid-Base Extraction

- Extraction is a **purification** method take advantage of the **different solubilities** of acids and their salts



- Impurities can be removed from a carboxylic acid using acid–base extractions

Acid-Base Extraction - Example

How can you separate a mixture of butanoic acid, butanamine and benzene?