CHAPTER 4

THE ACID-BASE REACTION

Contents:

- Acid and Base
- Acid-base equilibrium
- Acidity and Basicity

4.1 Definitions

⇒ **Bronsted-Lowry definition**

acid -- proton (H^+) donor; base -- proton acceptor

H-A -- an acid (eg HX, H_2O, ROH, RNH_2, RCH_3)

B: -- a base (eg RNH_2, ROH, H_2O (amphoteric), RNH^-)

Lewis definition

acid -- e^- pair acceptor

base -- e^- pair donor

4.2 The Acid-Base Equilbrium

Acidity constant is in the range of 10^{10}~ 10^{-50}, too large or small to be understood. Therefore logarithmic scale pK_a is used and defined as

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

Then pK_a is from -10~ 50, much easier to be understood.

Using K_a or pK_a value, acidity could be expected.

General acid-base reaction

Ex)

$$\mathrm{H{-}Br} \quad + \quad \mathrm{H_2O} \quad \rightleftharpoons \quad \mathrm{Br}^{\ominus} \quad + \quad \mathrm{H_3O}^{\oplus}$$

HBr; K_a =10^9, pK_a = -9 H_3O^+; K_a =55, pK_a = -1.74

K = 1.8 x 10^7 (right side is favored)

H_3O^+ is a weaker acid and Br^- is aweaker base.

Scale showing some acid and base strength

Free Energies of Reactant and Products

4.3 Rate of Acid-Base Reaction

Reaction rate depends on

1) Stereoelectronic requirement for the collision of the two molecules

ex) NH_3 + $HO_2C\text{-}CH_3$

Stereoelectronic requirement;
The orientation required for the orbitals of the reactants

Including this, most of the acid-base reactions satisfy the Stereoelectronic requirement

Reaction rate depends on

2) Activation energy

ex) HBr + H_2O

Including this, most of the acid-base reactions have very small activation energies.

Therefore most acid-base reactions are very fast.

RDS for most organic reaction is not the acid-base reaction

4.4 Effect of atoms bonded to H on Acidity

Ex)

N is More electronegative; NH_3 is more acidic

➢ **In the same period**

- **Acidity of HA ↑ as electronegativity of A ↑**
- **Why? stability of $A:^-$ ($^-:CH_3 < {}^-:NH_2 < HO:^- < F:^-$) ↑**

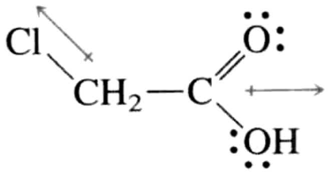
  bacisity of conj base ↓

In the same group (column)

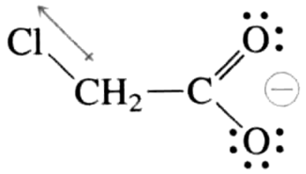
1. Acidity of HA ↑ from top to bottom
2. Why? size of A ↑ (loosely bound); overweigh E

4.5 Inductive Effect

Ex)



Less stable than acetic acid



more stable than acetic acid

See Fig 4.6 in p 117

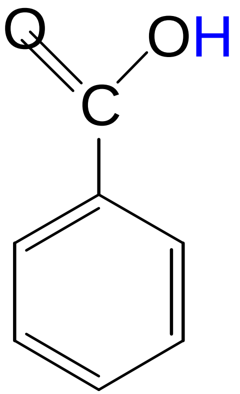
electron-withdrawing group

- pulls more electron density than hydrogen does
- $CH_3COOH < ClCH_2COOH < Cl_3CCOOH$
- destabilize an electron-poor site (make acid stronger)
- stabilize an electron-rich site (make conj base weaker)

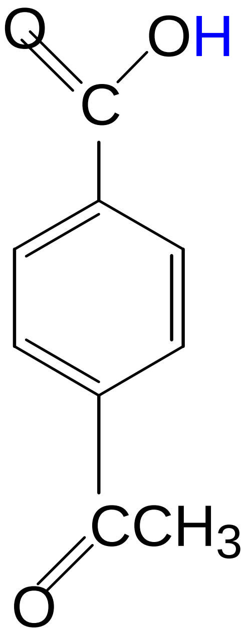
inductive electron-withdrawing groups → **Increase the acidity**

inductive electron-donating groups → **decrease the acidity**

4.6 Hydrogen Bonding

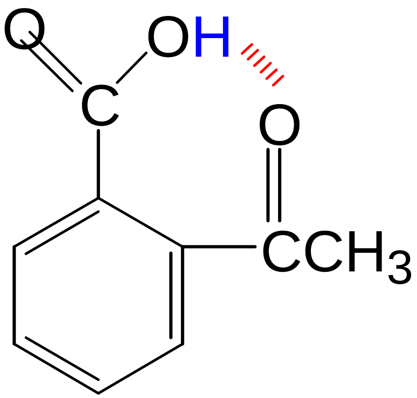


pK_a = 4.19



3.70

Electron withdrawing effect



4.13

Electron withdrawing + H-bonding effect

When acidic hydrogen is intramolecularly H-bonded, the acidity decreases.

4.7 hybridization

sp^3 (25% s orbital) **sp^2 (33% s orbital)** **sp (50% s orbital)**

- **The more *s* character**
  - **the lower energy orbital (see Fig 4.8 p. 120)**
  - **the more electronegative carbon**
  - **the more stable conjugate base (stronger acid)**

$CH_3CH_2^- < CH_2{=}CH^- < CH{\equiv}C^-$

4.8 Resonance

1) delocalize and stabilize conjugate base

2) make an acid stronger

Resonance +
electron
withdrawing (CO)
effect

Examples

Ethanol vs Phenol vs benzyl alcohol

CH_2 group acts as insulator of the resonance

Examples

Phenols with nitro groups

Electron withdrawing
+resonance stabilization

More electron
withdrawing (closer)
+ less resonance
stabilization

More electron
withdrawing (closer),
+ similar resonance
stabilization
+ H-bonding

Examples

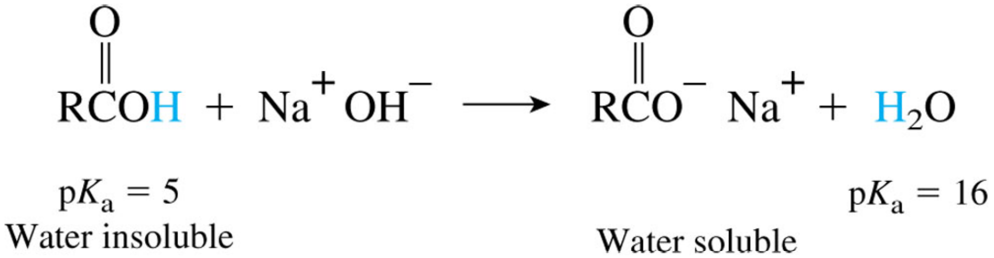
Conjugate acids of aniline derivatives

Acidity of C-H

4.9 Tables of Acids and Bases

- See table 4.2, 4.3, and 4.4

4.10 Acidity and Basicity of Functional Groups and Solvents



$$R\overset{O}{\overset{\|}{C}}OH + Na^{+}OH^{-} \longrightarrow R\overset{O}{\overset{\|}{C}}O^{-}\ Na^{+} + H_2O$$

$pK_a = 5$
Water insoluble

Water soluble

$pK_a = 16$

$+ \quad K^{+}HCO_3^{-} \longrightarrow \ ?$

Potassium bicarbonate

H_2CO_3
$pK_a = 6.35$

Carbonic acid

⇒ **Insoluble amine + HCl = soluble salt**

⇒ **Separation & isolation of**

Both are water in soluble

⇒ **Reaction solvents: the leveling effect**