Organic Chemistry Concepts LOKT.09.051

Acids and bases

CHAPTER 6

Brønsted - Lowry definition

- **Acids – donors of proton**
- **Bases – acceptors of proton**
- Commonly fast exchange reaction
- Slow, if dissociation of C-H bond is involved

Johannes Nicolaus Brønsted **(1879-1947)**

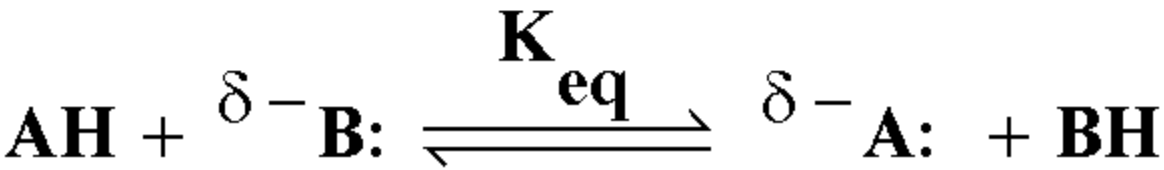
Some Remarks on the Concept of Acids and Bases.

J. N. Brønsted, Recueil des Travaux

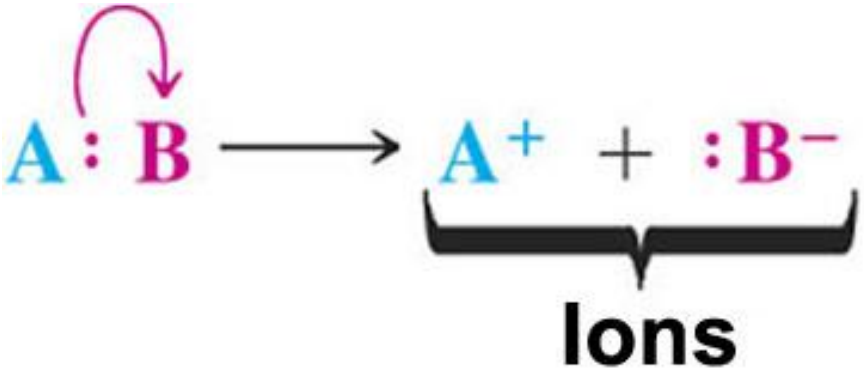
Thomas Martin Lowry (1874-1936)


AH
H+ + :A-


B: + H+
BH+


Keq
AH + δ− B:
δ− A: + BH

This is a special case of ionic reactions



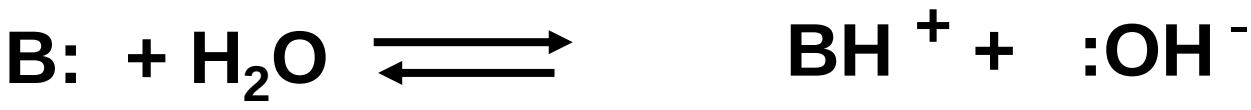
Bond heterolysis

$$AH + H_2O: \underset{}{\overset{K_{eq}}{\rightleftharpoons}} {}^{-}A: + {}^{+}H_3O$$

$$K_{eq} = \frac{[H_3O^+] \quad [^-A:]}{[H_2O] \quad [AH]}$$

$$K_{eq}[H_2O] = K_a = \frac{[H_3O^+] \quad [^-A:]}{[AH]}$$

$$-\log K_a = pK_a = -\log \frac{[H_3O^+] \quad [^-A:]}{[AH]}$$



$$K_{eq} = \frac{[BH^+]\quad[:OH^-]}{[H_2O]\quad[\ B:]}$$

$$K_{eq}\,[H_2O] = K_b = \frac{[BH^+]\quad[:OH^-]}{[B:]}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_{eq} = \frac{[H_3O^+]\ [OH^-]}{[H_2O]\ [H_2O]}$$

$$K_{eq}\,[H_2O]\,[H_2O] = K_W$$

$$K_w = [H_3O^+]\ [OH^-] = 1x\ 10^{-14}$$

$$-\log K_w = -\log[H_3O^+] - \log[OH^-] = 14$$

$$pH + pOH = 14$$

Three mechanisms of proton transfer

$$AH + :B^{\Delta-} \rightleftarrows AH\ldots.:B^{\Delta-}$$

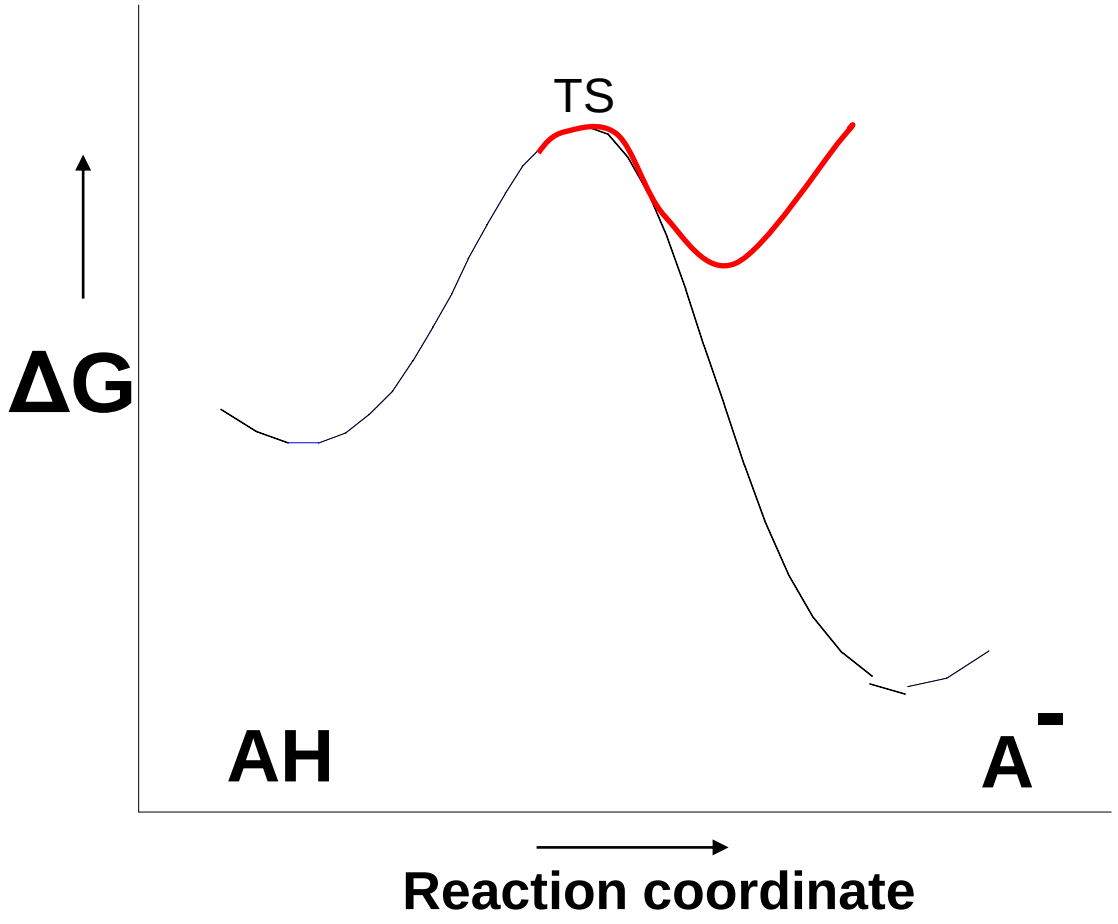
$$AH\ldots.:B^{\Delta-} \rightleftarrows {}^{\Delta-}A:\ldots.HB$$

$${}^{\Delta-}A:\ldots.HB \rightleftarrows {}^{\Delta-}A: + HB^{\Delta-}$$

Acid strength

$$K_a = \frac{[H^+]\ [^-A:]}{[AH]}$$

$$pK_a = pH + \log([AH]/[^-A:])$$


TS
ΔG
AH
A-
Reaction coordinate

pKa (relatively, in water)

- **HF** **3.2** (4.0)
- **H_2O** **15.7** (3.5)
- **NH_3** **38** (3.0)
- **H_2** **35** (2.1)
- **CH_4** **48** (2.5)

$$K_a = [H^+][A^-]/[HA]$$

$$pKa = pH + \log([HA]/[A^-])$$

pKa (in water)

- **HI** **-10** (2.5)
- **HBr** **- 9** (2.8)
- **HCl** **- 7** (3.0
- **HF** **3.2** (4.0)

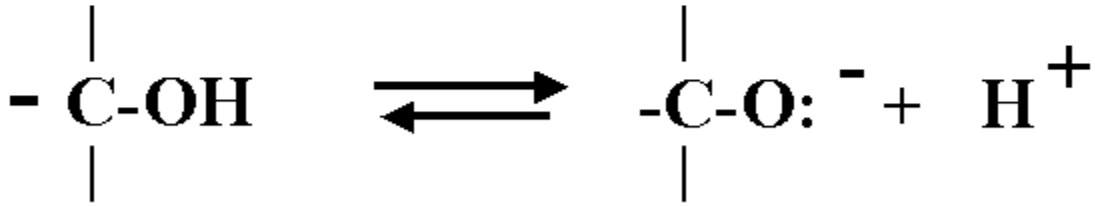
- H_2S **7.0** (2.5)
- H_2O **15.7** (3.5)

$$K_a = [H^+][A^-]/[HA]$$

Functional group acidity

- OH
- SH
- NH
- CH

OH acids



- HCOOH 3.75
- C_6H_5OH 10
- CH_3OH 15.2

NH acids

- H_2O 15.7
- H_3O^+ -1.7
- C_6H_5OH 10
- $C_6H_5OH_2^+$ -6.4

- **NH_3 38**
- **NH_4^+ 9.2**
- **$C_6H_5NH_2$ 38**
- **$C_6H_5NH_3^+$ 4.5**
- **$(C_6H_5)_2NH$ 25**
- **$(C_6H_5)_2NH_2^+$ 1**
- **$4\text{-}NO_2\text{-}C_6H_4NH_3^+$ 1**

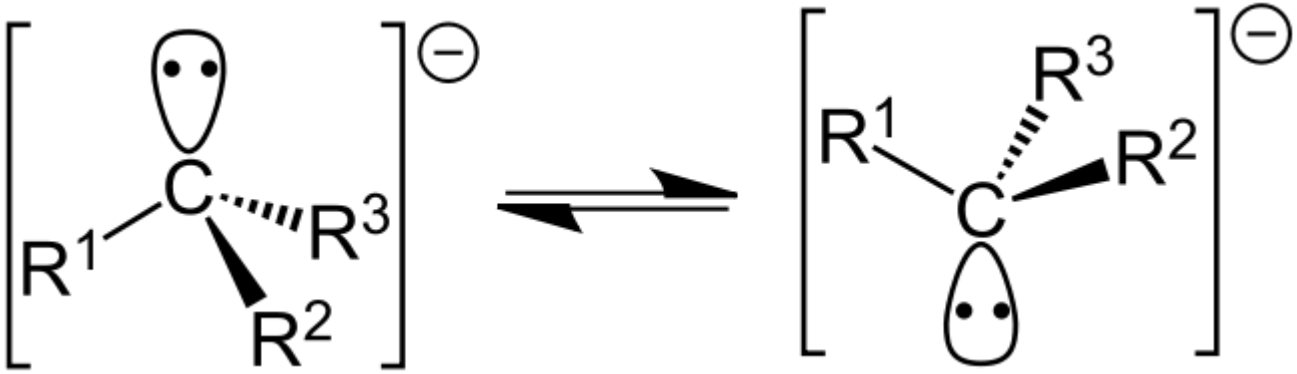
SH acids

- H_2O 15.7
- H_3O^+ -1.7
- C_2H_5OH 16
- $C_2H_5OH_2^+$ -2
- C_6H_5OH 10
- $C_6H_5OH_2^+$ -6.4

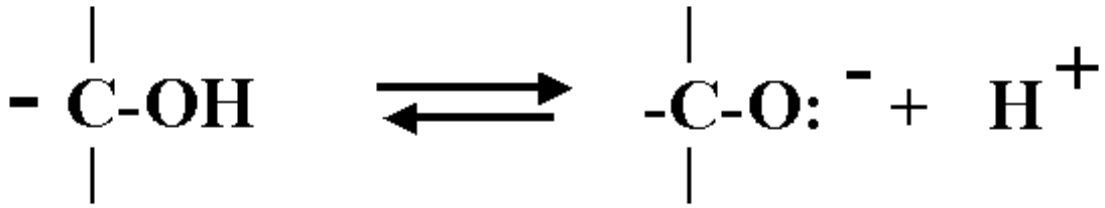
- **H_2S 7.0**
- **C_2H_5SH 10.5**
- **$C_2H_5SH_2^+$ -7**
- **C_6H_5SH 7.8**

CH acids

Carbon anion or **carbanion**

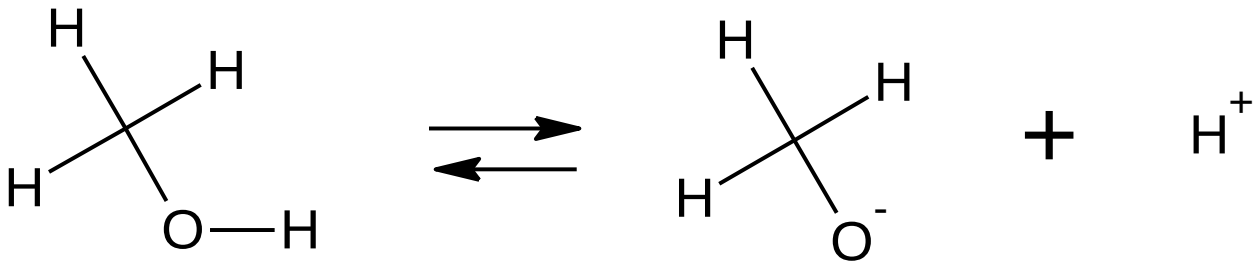

R1
C
R3
R2
R3
R1
R2
C

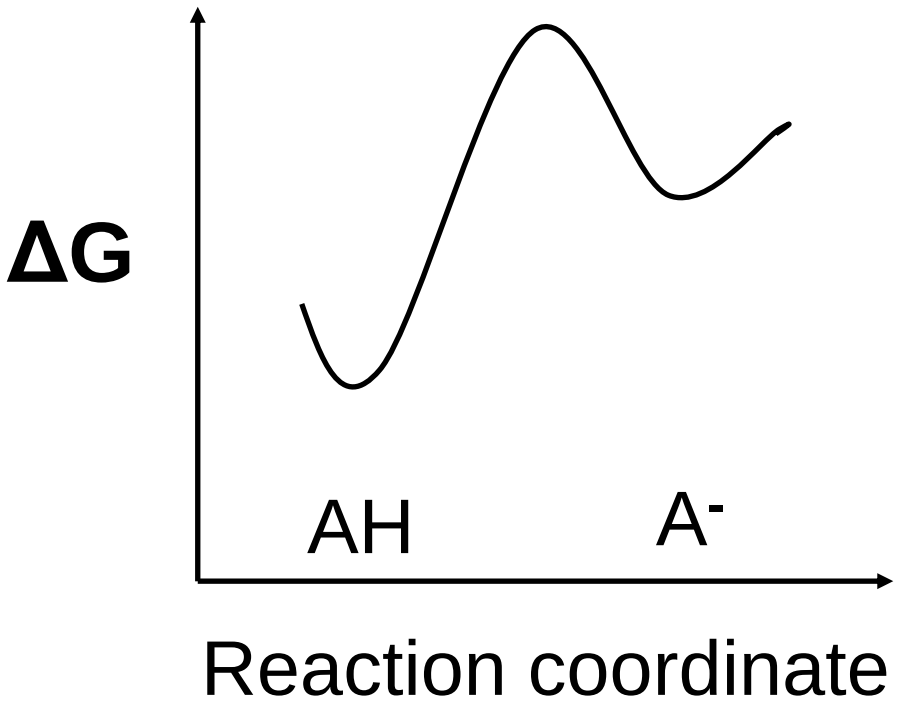
OH acids



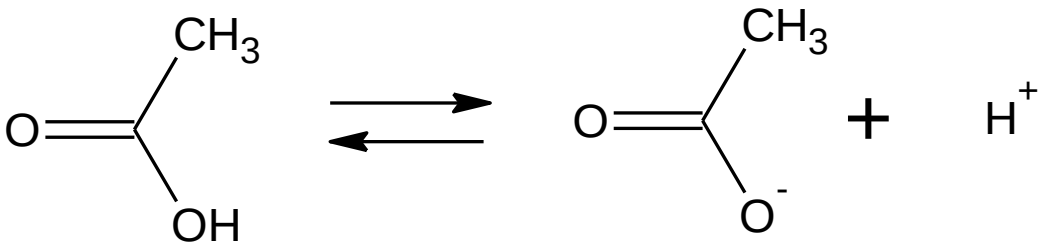
- HCOOH 3.75
- C_6H_5OH 10
- CH_3OH 15.2

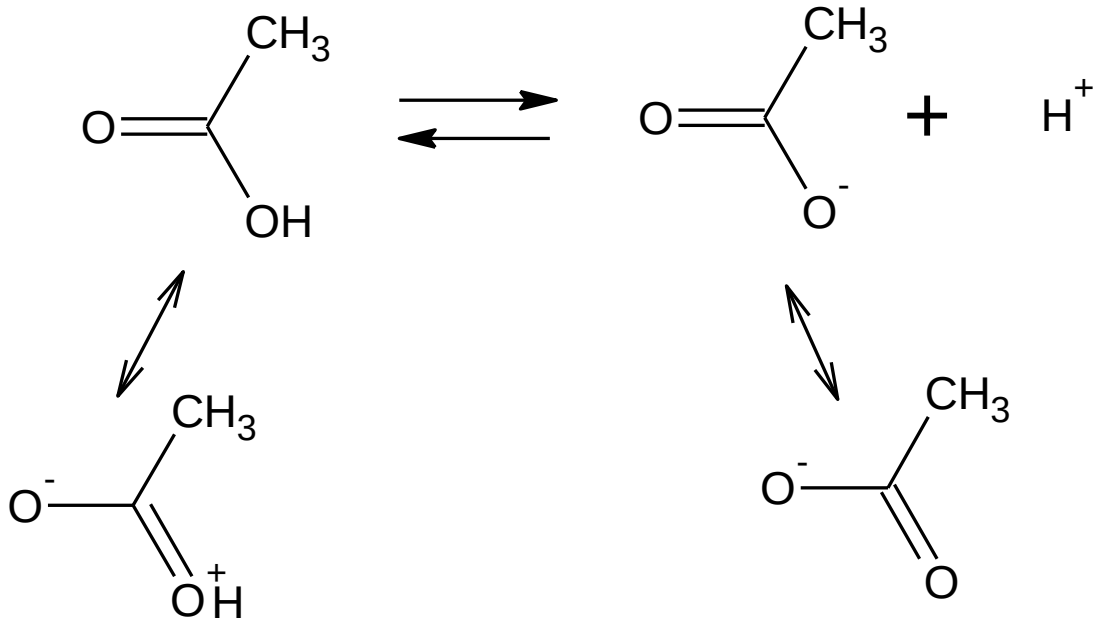
$pK_a = 15.2$

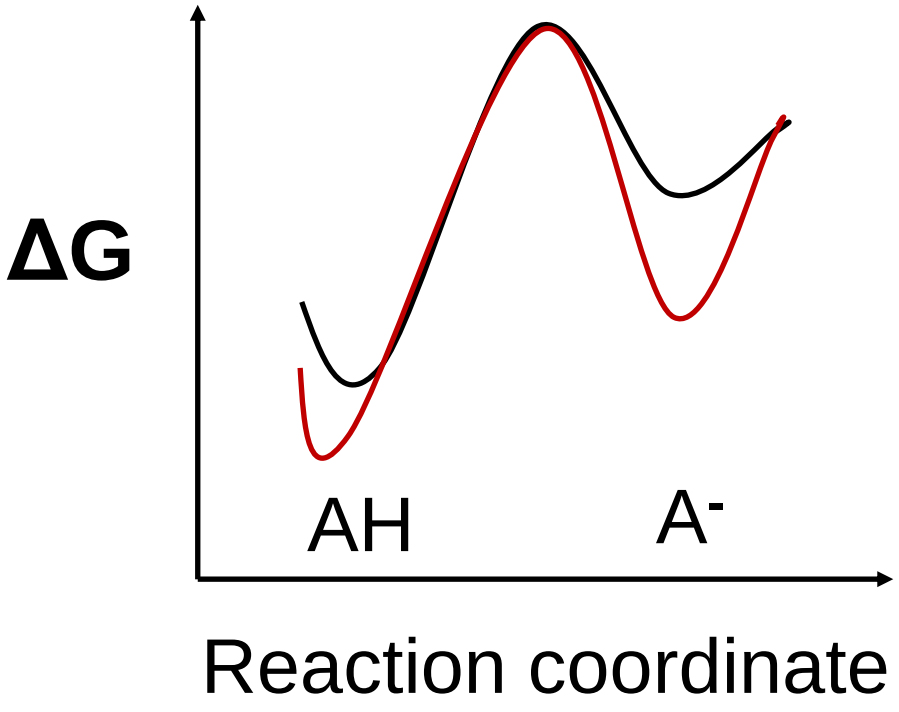



ΔG
AH
A-
Reaction coordinate

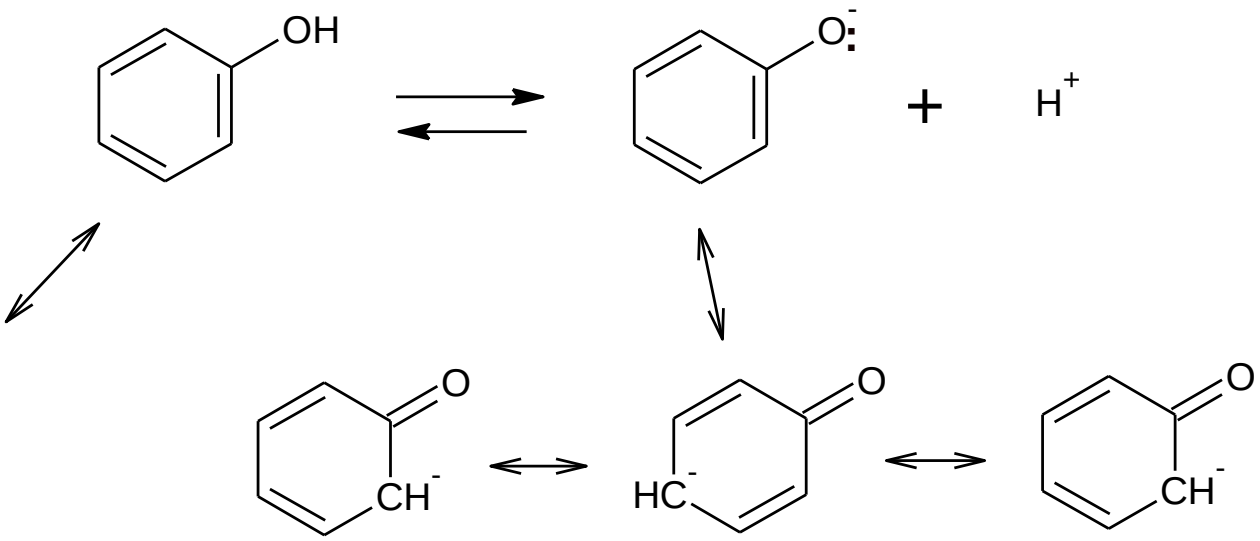
$pK_a = 4.8$



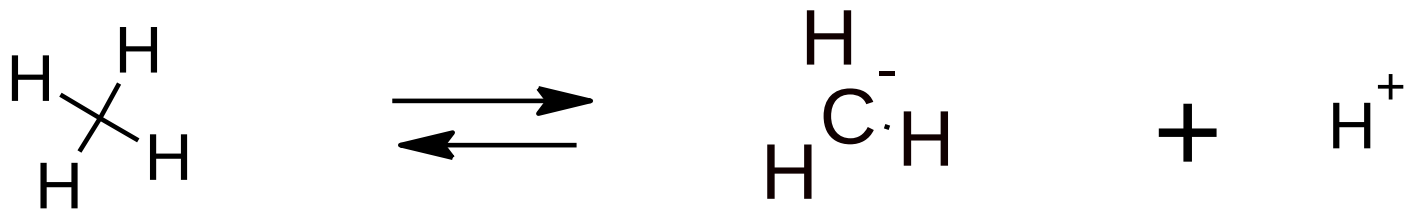

CH3
O
OH
CH3
O
O-
+
H+
CH3
O-
OH+
CH3
O-
O


ΔG
AH
A-
Reaction coordinate

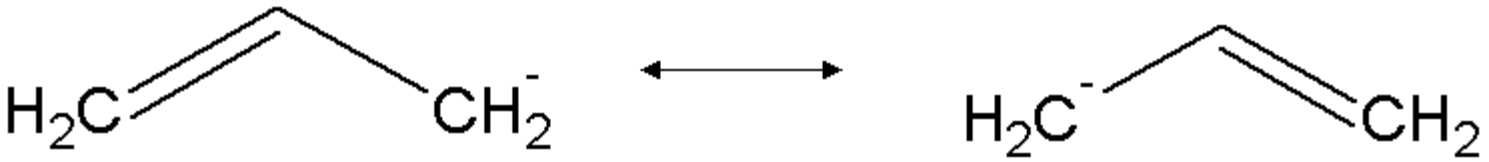
$pK_a = 10$



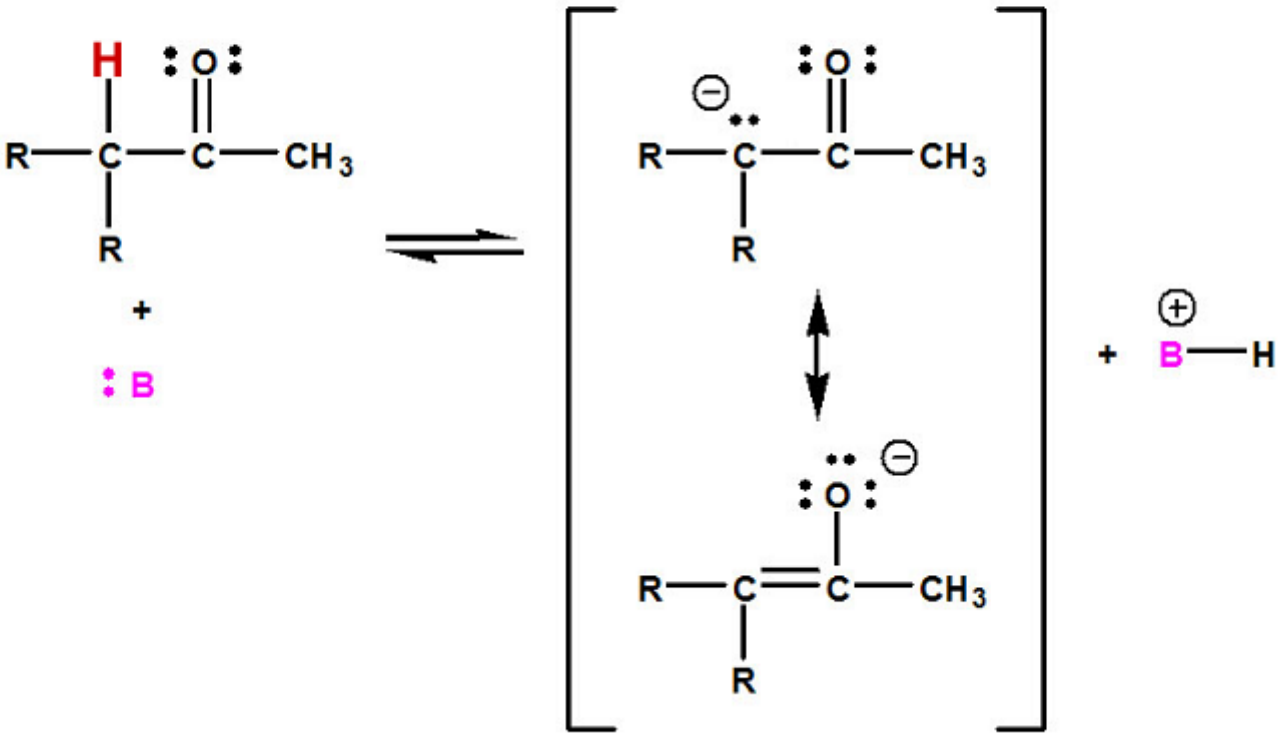
Carbanion stability
pK_a 45



Carbanion stability



α- hydrogen acidity

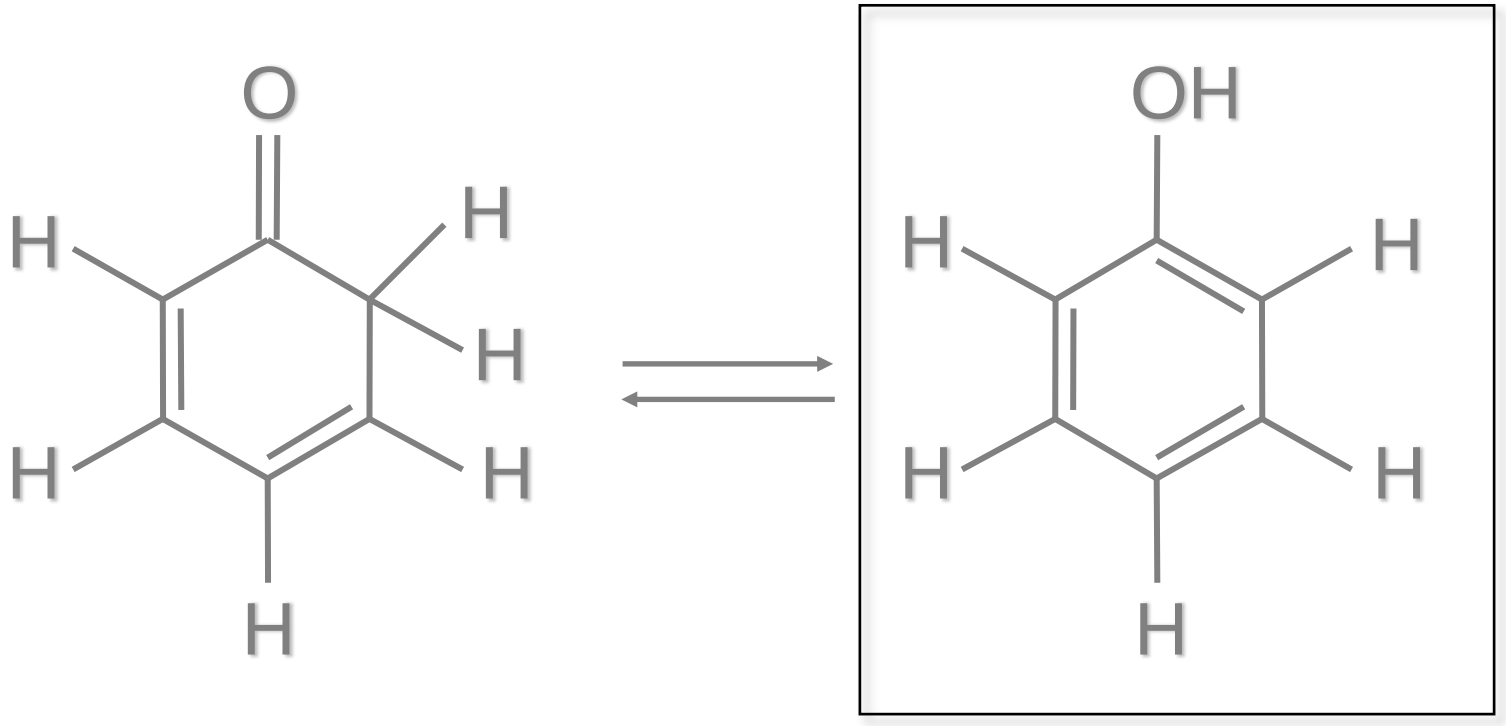


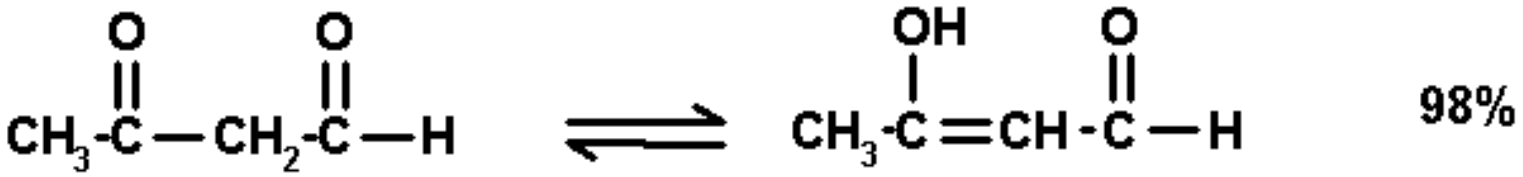
Enols or alkenols

Keto - form Enol

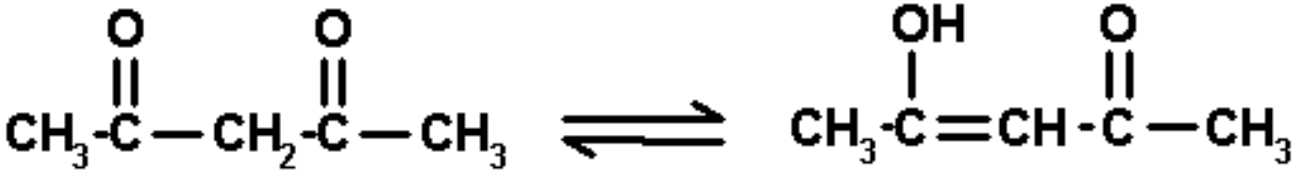
Ketones are stable!

Stable enol

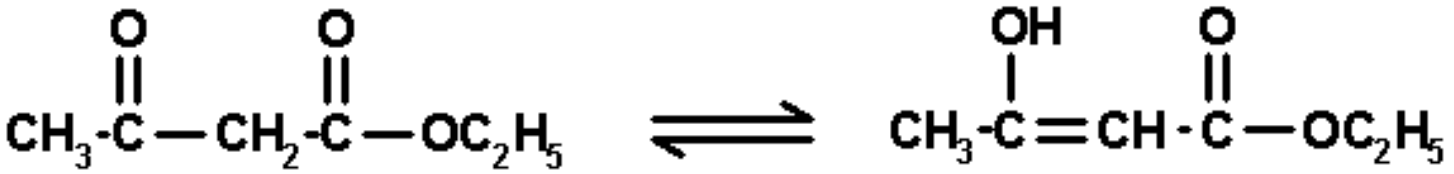



O
O
CH3-C—CH2-C—H
OH
O
CH3-C=CH-C—H

98%


O
O
CH3-C—CH2-C—CH3
OH
O
CH3-C=CH-C—CH3

80%


O
O
CH3-C—CH2-C—OC2H5
OH
O
CH3-C=CH-C—OC2H5

8%