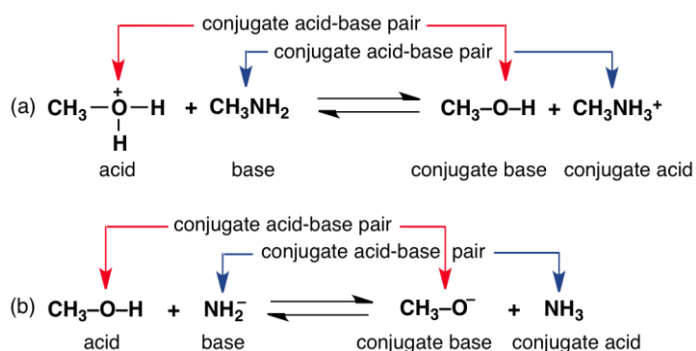


Solutions to Exercises, Chapter 6

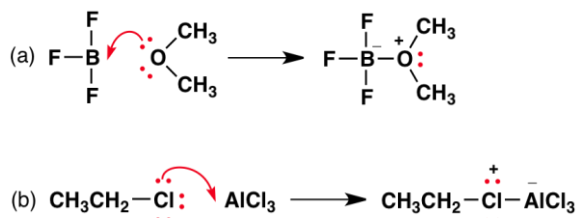
6.1 (a) Br^- (b) HCO_2^- (c) CH_3S^- (d) HSO_4^- (e) CH_3NH^- 6.2 (a) CH_3OH_2^+ (b) CH_3NH_3^+ (c) HCl (d) CH_3OH (e) $(\text{CH}_3)_2\text{C}=\text{NH}_2^+$

6.3



6.4 (a) Lewis base (b) acid (c) base (d) acid (e) acid

6.5

6.6 (a) $K_a = 10^{-5}$ (b) $K_a = 10^{-10}$ Acid (a) is stronger than (b).

$$\begin{aligned}
 6.7 \quad (a) \quad K &= [\text{HCO}_2^-][\text{CH}_3\text{NH}_3^+]/[\text{HCO}_2\text{H}][\text{CH}_3\text{NH}_2] \\
 &= ([\text{HCO}_2^-][\text{H}_3\text{O}^+]/[\text{HCO}_2\text{H}])([\text{CH}_3\text{NH}_3^+]/[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]) \\
 &= K_a(\text{HCO}_2\text{H})/K_a(\text{CH}_3\text{NH}_3^+) = 10^{-3.75}/10^{-10.64} = 10^{6.89} \gg 1
 \end{aligned}$$

The equilibrium is far towards the right.

$$\begin{aligned}
 (b) \quad K &= [\text{PhCO}_2^-][\text{PhNH}_3^+]/[\text{PhCO}_2\text{H}][\text{PhNH}_2] \\
 &= ([\text{PhCO}_2^-][\text{H}_3\text{O}^+]/[\text{PhCO}_2\text{H}])([\text{PhNH}_3^+]/[\text{PhNH}_2][\text{H}_3\text{O}^+]) \\
 &= K_a(\text{PhCO}_2\text{H})/K_a(\text{PhNH}_3^+) = 10^{-4.20}/10^{-4.60} = 10^{0.4} \approx 2.5
 \end{aligned}$$

The equilibrium is somewhat towards the right.

$$\begin{aligned}
 6.8 \quad K &= [\text{A}^-][\text{BH}^+]/[\text{AH}][\text{B}] = ([\text{A}^-][\text{H}_3\text{O}^+]/[\text{AH}])([\text{BH}^+]/[\text{B}][\text{H}_3\text{O}^+]) \\
 &= K_a(\text{AH})/K_a(\text{BH}^+) \\
 \text{p}K &= -\log K = -\log\{K_a(\text{AH})/K_a(\text{BH}^+)\} = \text{p}K_a(\text{AH}) - \text{p}K_a(\text{BH}^+)
 \end{aligned}$$

6.9	pH 2	pH 7	pH 12
(a)	HCO_2H	HCO_2^-	HCO_2^-
(b)	NH_4^+	NH_4^+	NH_3
(c)	PhNH_3^+	PhNH_2	PhNH_2
(d)	HCN	HCN	CN^-

$$6.10 \quad (a) \text{ pH } 4.76 \quad (b) 5.06 \quad (c) 5.06 \quad (d) 4.46$$

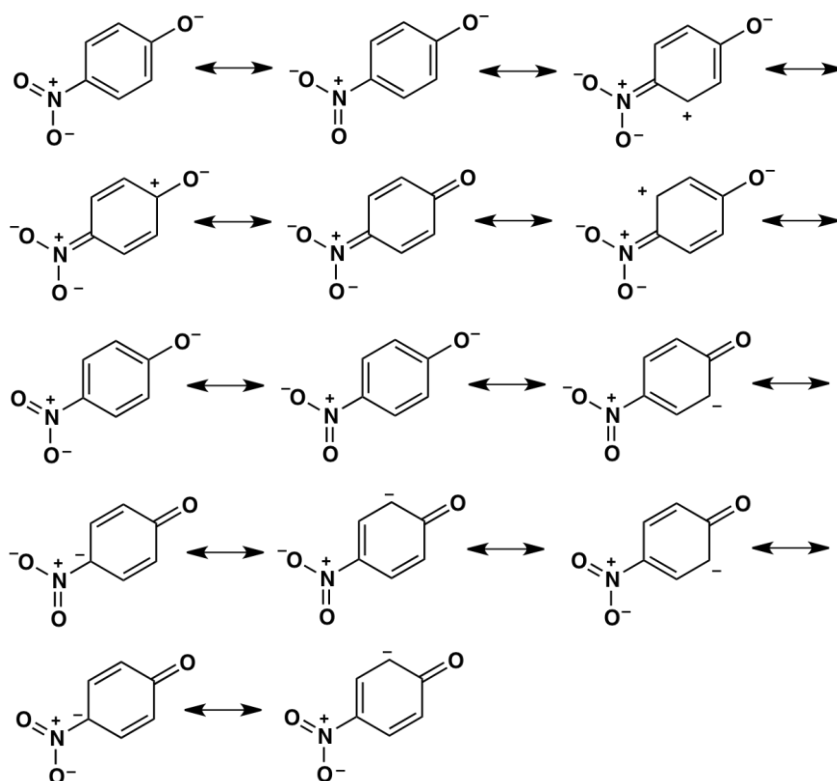
(Remember that $\log 2 = 0.30$.)

6.11 Ethanethiol is more acidic than ethanol. Sulfur is an element of the third period while oxygen is in the second period of the periodic table. The S–H bond is weaker than the O–H bond, so EtSH is a stronger acid than EtOH.

6.12 F is more electron withdrawing than OH.

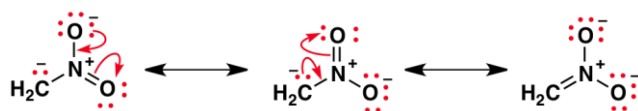
Acidities increase in the order: $\text{CH}_3\text{CO}_2\text{H} < \text{HOCH}_2\text{CO}_2\text{H} < \text{FCH}_2\text{CO}_2\text{H}$

6.13

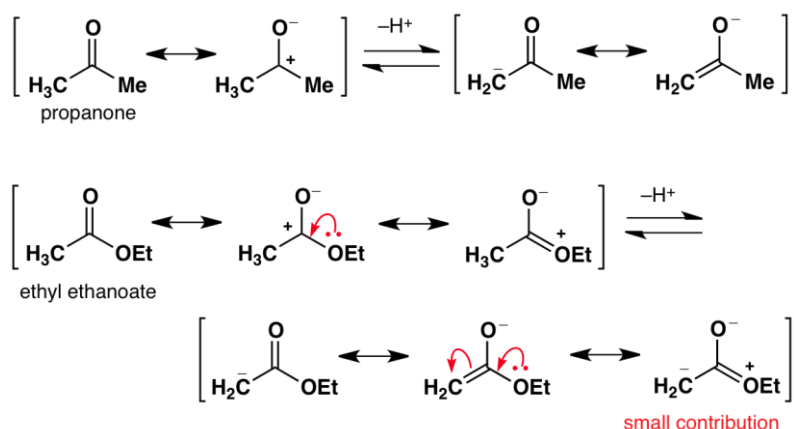


6.14 The pK_a of 9-phenylfluorene is much lower than the value for triphenylmethane because the bond joining two of the benzene rings in 9-phenylfluorene substantially improves the degree of coplanarity of the conjugate base and hence increases its resonance stabilization.

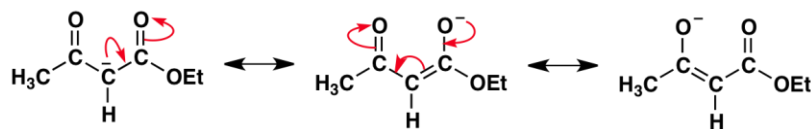
6.15



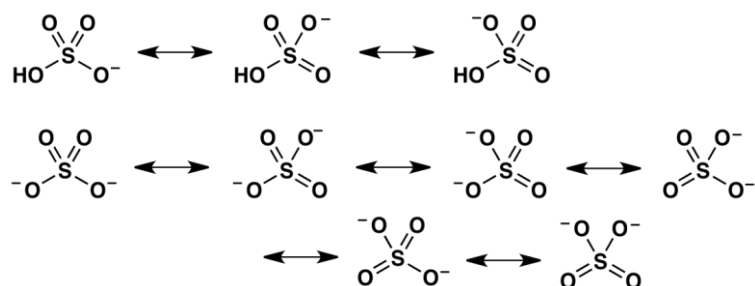
6.16 The main resonance forms of propanone and ethyl ethanoate are shown below together with those of their conjugate bases, which are enolate anions. Propanone and its conjugate base both have two resonance contributors, but neither of those of the enolate involve charge separation, so its resonance stabilization will be greater. Ethyl ethanoate and its conjugate base also have the same number of resonance contributors, three each. However, the third contributor using the lone pair on the ethoxy oxygen will be less significant in the enolate than in the ethyl ethanoate; consequently, the ethanoate now has greater resonance stabilization than the enolate, so ethyl ethanoate is less acidic (greater pK_a) than propanone.



6.17 The C2 hydrogens are the most acidic, and the conjugate base is stabilized by resonance involving two carbonyl groups compared with just one in ethyl ethanoate.

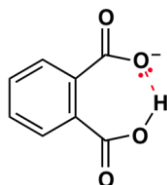


6.18



(Note that hydrogensulfate and sulfate are tetrahedral.)

6.19 The mono-anion of phthalic acid can form an intramolecular hydrogen bond which is a stabilizing feature. This enhances the acidity of phthalic acid but inhibits the further dissociation to give the dianion. There is no such effect for terephthalic acid so the difference between its two pK_a values is smaller than for phthalic acid.



6.20

