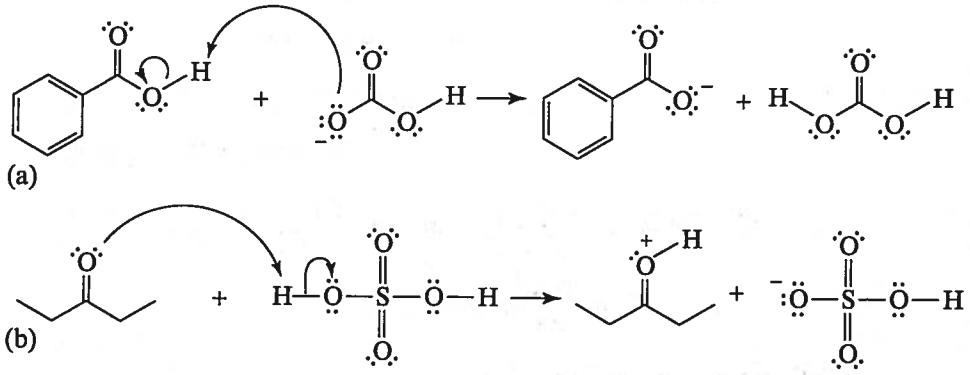
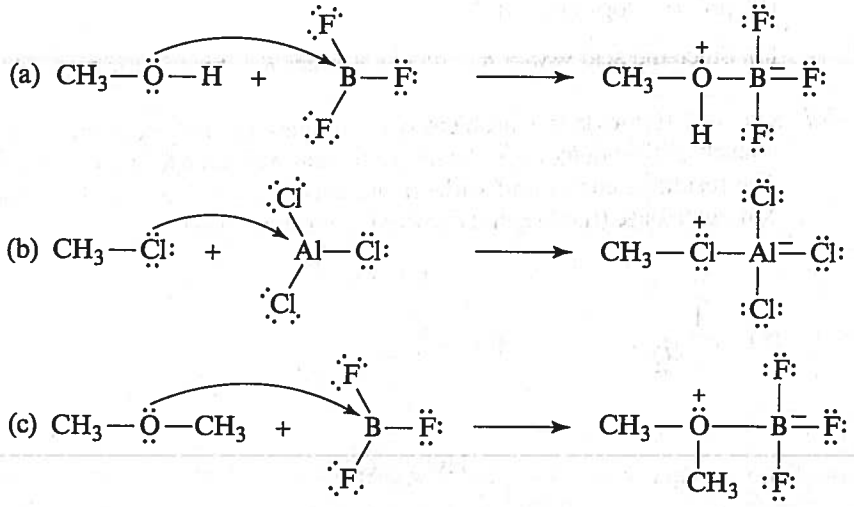
3 ACIDS AND BASES: AN INTRODUCTION TO ORGANIC REACTIONS AND THEIR MECHANISMS

SOLUTIONS TO PROBLEMS

3.1

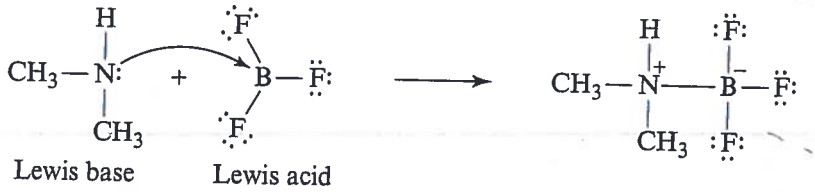


3.2



3.3 (a) Lewis base
(b) Lewis acid
(c) Lewis base
(d) Lewis base
(e) Lewis acid
(f) Lewis base

3.4



3.5 (a) $K_a = \dfrac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = 1.77 \times 10^{-4}$

Let $x = [H_3O^+] = [HCO_2^-]$ at equilibrium

then, $0.1 - x = [HCO_2H]$ at equilibrium

but, since the K_a is very small, x will be very small and $0.1 - x \simeq 0.1$

Therefore,

$$\frac{(x)(x)}{0.1} = 1.77 \times 10^{-4}$$

$$x^2 = 1.77 \times 10^{-5}$$

$$x = 0.0042 = [H_3O^+] = [HCO_2^-]$$

(b) % Ionized $= \dfrac{[H_3O^+]}{0.1} \times 100$ or $\dfrac{[HCO_2^-]}{0.1} \times 100$

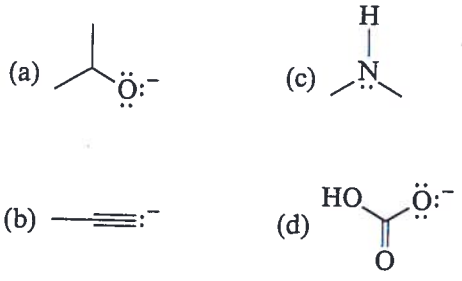
$$= \frac{.0042}{0.1} \times 100 = 4.2\%$$

3.6 (a) $pK_a = -\log\ 10^{-7} = -(-7) = 7$

(b) $pK_a = -\log\ 5.0 = -0.7$

(c) Since the acid with a $K_a = 5$ has a larger K_a, it is the stronger acid.

3.7 One way to tackle this problem is to compare the pK_a values for the protonated species of each of the choices (i.e. the molecule that would be formed if each behaved as a base). The resultant compound with the higher pK_a of the two is the weaker acid; hence, its conjugate base (the original choice) is a stronger base.

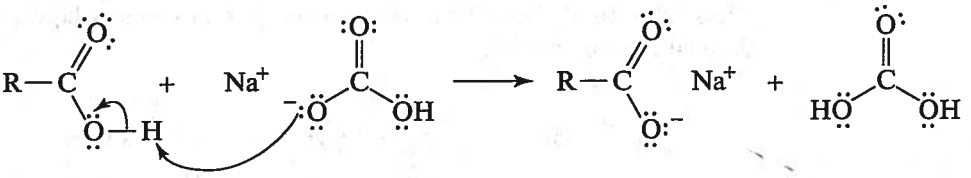


3.8 The pK_a of the methylaminium ion is equal to 10.6 (Section 3.6C). Since the pK_a of the anilinium ion is equal to 4.6, the anilinium ion is a stronger acid than the methylaminium ion, and aniline ($C_6H_5NH_2$) is a weaker base than methylamine (CH_3NH_2).

3.9



3.10



3.11 (a) Negative. Because the atoms are constrained to one molecule in the product, they have to become more ordered.

(b) Approximately zero.

(c) Positive. Because the atoms are in two separate product molecules, they become more disordered.

3.12 (a) If $K_{eq} = 1$

then,

$$\log K_{eq} = 0 = \frac{-\Delta G^\circ}{2.303RT}$$

$$\Delta G^\circ = 0$$

(b) If $K_{eq} = 10$

then,

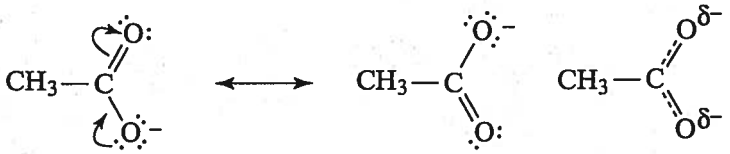
$$\log K_{eq} = 1 = \frac{-\Delta G^\circ}{2.303RT}$$

$$\Delta G^\circ = -(2.303)(0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = -5.71 \text{ kJ mol}^{-1}$$

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = \Delta H^\circ = -5.71$ kJ mol^{-1} if $\Delta S^\circ = 0$

3.13 Structures **A** and **B** make equal contributions to the overall hybrid. This means that the carbon-oxygen bonds should be the same length and that the oxygens should bear equal negative charges.



A **B** hybrid

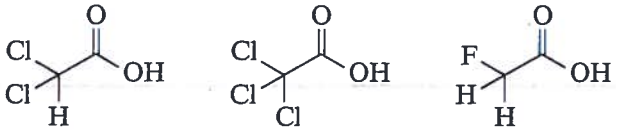
3.14 (a) $CHCl_2CO_2H$ would be the stronger acid because the electron-withdrawing inductive effect of *two chlorine atoms* would make its hydroxyl proton more positive. The electron-withdrawing effect of the two chlorine atoms would also stabilize the dichloroacetate ion more effectively by dispersing its negative charge more extensively.

(b) CCl_3CO_2H would be the stronger acid for reasons similar to those given in (a), except here there are three versus two electron-withdrawing chlorine atoms involved.

(c) CH_2FCO_2H would be the stronger acid because the electron-withdrawing effect of a fluorine atom is greater than that of a bromine atom (fluorine is more electronegative).

(d) CH_2FCO_2H is the stronger acid because the fluorine atom is nearer the carboxyl group and is, therefore, better able to exert its electron-withdrawing inductive effect.

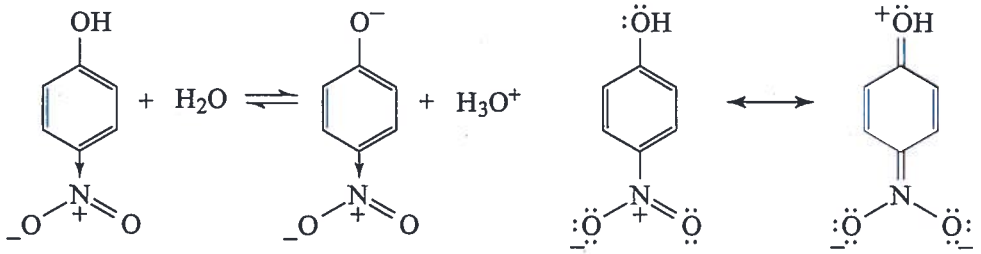
(*Remember:* Inductive effects weaken steadily as the distance between the substituent and the acidic group increases.)



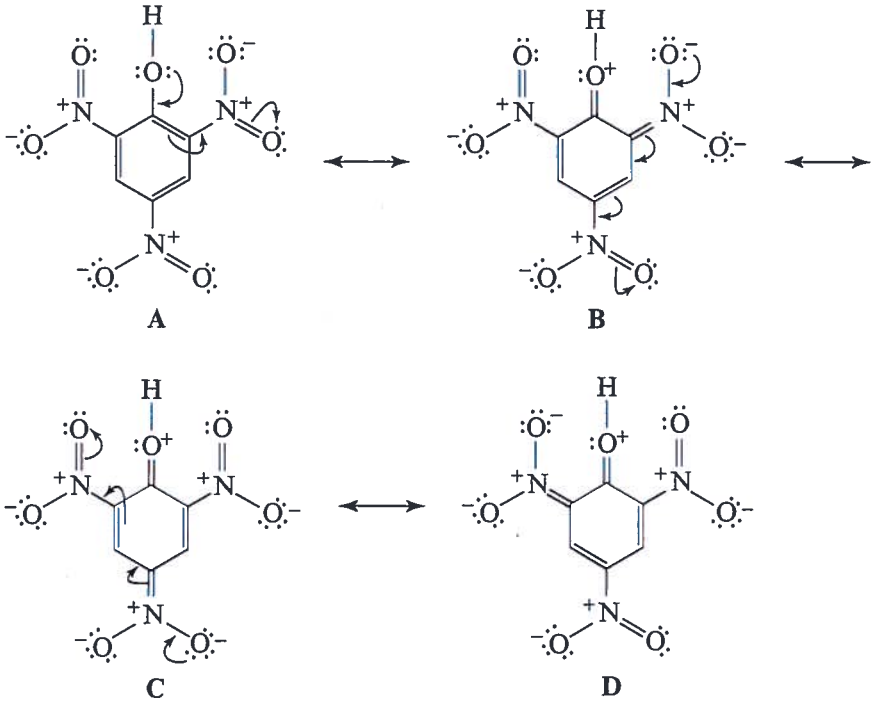
(a) (b) (c) and (d)

3.15 The inductive effect of an electron-withdrawing group such as a nitro group changes the charge distribution in the molecule so as to decrease the electron density of the ring and the oxygen, causing the proton to be held less strongly; it can also stabilize the phenoxide by dispersing its negative charge. Moreover, through resonance, a positive charge can be placed on the hydroxyl oxygen. These collective effects make the proton to be held much less strongly than in phenol, and hence 4-nitrophenol is more acidic.

Inductive contribution: *Resonance contribution:*



As shown below in resonance structures **A-D** for 2,4,6-trinitrophenol (picric acid), these effects are more pronounced since there are now three nitro groups that can make the hydroxyl oxygen dramatically more positive, and its proton is much more acidic as a result.



A **B**

C **D**

3.16 Dissolve the mixture in a solvent such as CH_2Cl_2 (one that is immiscible with water). Using a separatory funnel, extract this solution with an aqueous solution of sodium bicarbonate. This extraction will remove the benzoic acid from the CH_2Cl_2 and transfer it (as sodium benzoate) to the aqueous bicarbonate solution. Acidification of this aqueous extract will cause benzoic acid to precipitate; it can then be separated by filtration and purified by recrystallization.

The CH_2Cl_2 solution can now be extracted with an aqueous solution of sodium hydroxide. This will remove the 4-methylphenol (as its sodium salt). Acidification of the aqueous extract will cause the formation of 4-methylphenol as a water-insoluble layer. The 4-methylphenol can then be extracted into ether, the ether removed, and the 4-methylphenol purified by distillation.

The CH_2Cl_2 solution will now contain only toluene and (CH_2Cl_2). These can be separated easily by fractional distillation.

3.17 All compounds containing oxygen and most compounds containing nitrogen will have an unshared electron pair on their oxygen or nitrogen atom. These compounds can, therefore, act as bases and accept a proton from concentrated sulfuric acid. When they accept a proton, these compounds become either oxonium ions or ammonium ions, and having become ionic, they are soluble in the polar medium of sulfuric acid. The only nitrogen compounds that do not have an electron pair on their nitrogen atom are quaternary ammonium compounds, and these, already being ionic, also dissolve in the polar medium of concentrated sulfuric acid.

3.18 (a) $CH_3\ddot{O}-H + {}^{-}\!:H \xrightarrow{\text{methanol}} CH_3\ddot{O}:^{-} + H_2$

Stronger acid, $pK_a = 16$ — Stronger base (from NaH) — Weaker base — Weaker acid, $pK_a = 35$

(b) $CH_3CH_2\ddot{O}-H + {}^{-}\!:\ddot{N}H_2 \xrightarrow{\text{ethanol}} CH_3CH_2\ddot{O}:^{-} + :NH_3$

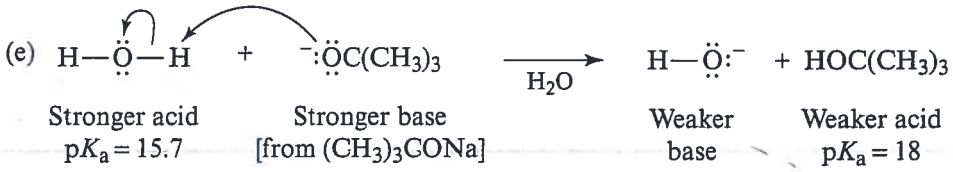
Stronger acid, $pK_a = 16$ — Stronger base (from $NaNH_2$) — Weaker base — Weaker acid, $pK_a = 38$

(c) $H-\ddot{N}(H)-H + {}^{-}\!:CH_2CH_3 \xrightarrow{\text{hexane}} {}^{-}\!:\ddot{N}H_2 + CH_3CH_3$

Stronger acid, $pK_a = 38$ — Stronger base (from CH_3CH_2Li) — Weaker base — Weaker acid, $pK_a = 50$

(d) $H-{}^{+}\!N(H)-H + {}^{-}\!:\ddot{N}H_2 \xrightarrow{\text{liq. } NH_3} :NH_3 + :NH_3$

Stronger acid, $pK_a = 9.2$ (from NH_4Cl) — Stronger base (from $NaNH_2$) — Weaker base — Weaker acid, $pK_a = 38$

(e) 

(f) No appreciable acid-base reaction would occur because HO^- is not a strong enough base to remove a proton from $(CH_3)_3COH$.

3.19 (a) $HC{\equiv}CH + NaH \xrightarrow[\text{hexane}]{} HC{\equiv}CNa + H_2$

(b) $HC{\equiv}CNa + D_2O \longrightarrow HC{\equiv}CD + NaOD$

(c) $CH_3CH_2Li + D_2O \xrightarrow[\text{hexane}]{} CH_3CH_2D + LiOD$

(d) $CH_3CH_2OH + NaH \xrightarrow[\text{hexane}]{} CH_3CH_2ONa + H_2$

(e) $CH_3CH_2ONa + T_2O \longrightarrow CH_3CH_2OT + NaOT$

(f) $CH_3CH_2CH_2Li + D_2O \xrightarrow[\text{hexane}]{} CH_3CH_2CH_2D + LiOD$

Problems

Brønsted-Lowry Acids and Bases

3.20 (a) $^-{:}\ddot{N}H_2$ (the amide ion)

(b) $H{-}\ddot{O}{:}^-$ (the hydroxide ion)

(c) $:H^-$ (the hydride ion)

(d) $H{-}C{\equiv}C{:}^-$ (the ethynide ion)

(e) $CH_3\ddot{O}{:}^-$ (the methoxide ion)

(f) $H_2\ddot{O}$ (water)

3.21 $^-{:}\ddot{N}H_2 > :H^- > H{-}C{\equiv}C{:}^- > CH_3\ddot{O}{:}^- \approx H{-}\ddot{O}{:}^- > H_2O$

3.22 (a) H_2SO_4

(b) H_3O^+

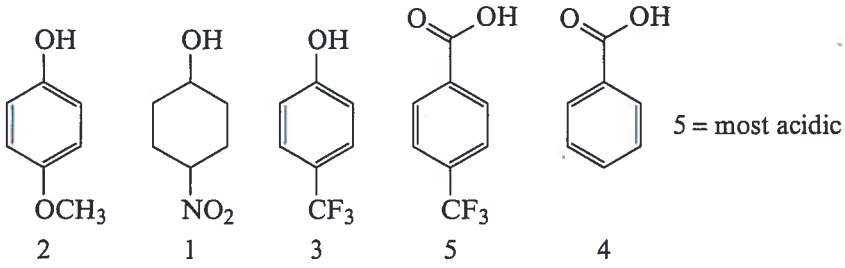
(c) $CH_3\overset{+}{N}H_3$

(d) NH_3

(e) CH_3CH_3

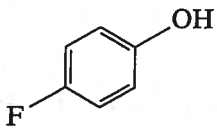
(f) CH_3CO_2H

3.23 $H_2SO_4 > H_3O^+ > CH_3CO_2H > CH_3\overset{+}{N}H_3 > NH_3 > CH_3CH_3$

3.24 

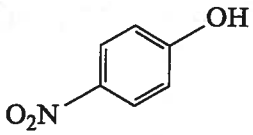
5 = most acidic

3.25 (a)



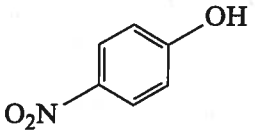
Fluorine is electron withdrawing; a methyl (alkyl) group is not

(b)



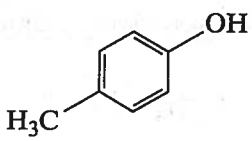
Nitro is electron withdrawing; a methyl (alkyl) group is not

(c)



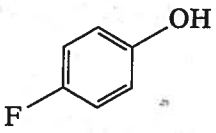
Only this nitro group can exert electron withdrawing though resonance

(d)



This compound is a phenol; the other is an alcohol

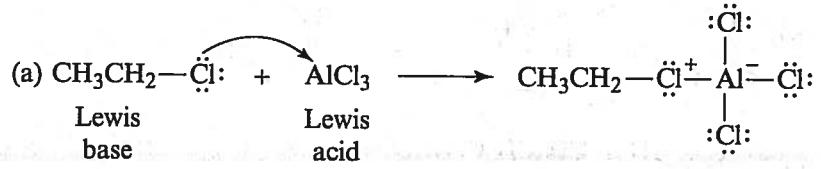
(e)



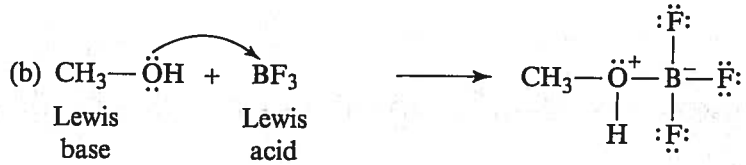
Fluorine is more electron withdrawing than bromine

Lewis Acids and Bases

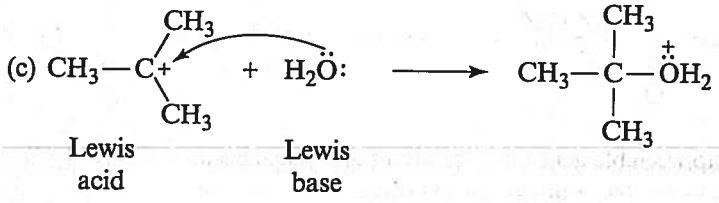
3.26 (a)



(b)



(c)

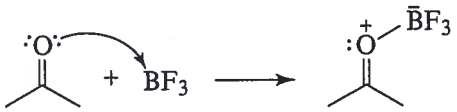


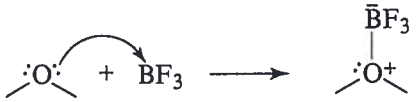
Curved-Arrow Notation

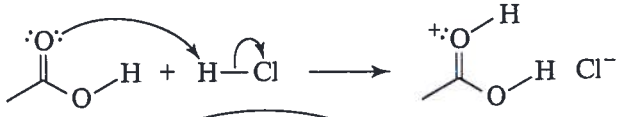
3.27 (a) 

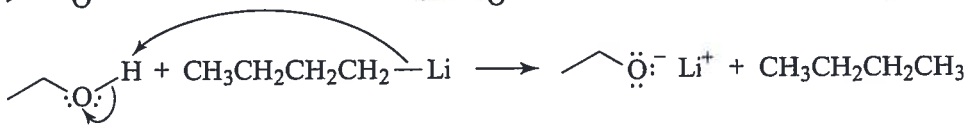
(b) 

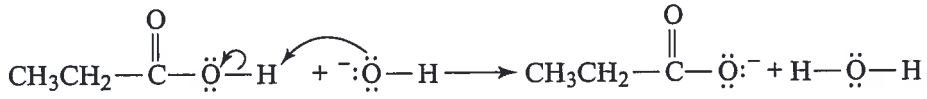
(c) 

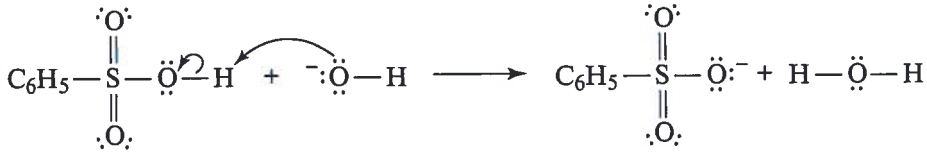
3.28 (a) 

(b) 

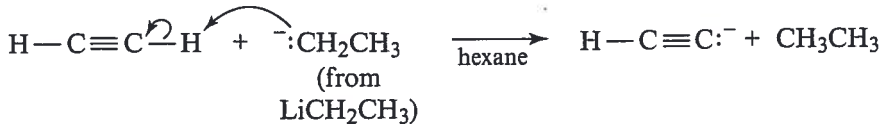
(c) 

(d) 

3.29 (a) 

(b) 

(c) No appreciable acid-base reaction takes place because CH_3CH_2ONa is too weak a base to remove a proton from ethyne.

(d) 

(e) $CH_3-CH_2-\ddot{O}-H + {}^{-}:CH_2CH_3 \xrightarrow[\text{hexane}]{} CH_3-CH_2-\ddot{O}:^{-} + CH_3CH_3$

(from $LiCH_2CH_3$)

Acid-Base Strength and Equilibrium

3.30 $CH_3CH_2-\ddot{O}-H + {}^{-}:C\equiv C-H \xrightarrow[\text{liq. } NH_3]{} CH_3CH_2-\ddot{O}:^{-} + H-C\equiv C-H$

3.31 (a) $pK_a = -\log 1.77 \times 10^{-4} = 4 - 0.248 = 3.75$

(b) $K_a = 10^{-13}$

3.32 (a) HB is the stronger acid because it has the smaller pK_a.

(b) Yes. Since A^- is the stronger base and HB is the stronger acid, the following acid-base reaction will take place.

$$\underset{\substack{\text{Stronger}\\\text{base}}}{A:^-} + \underset{\substack{\text{Stronger}\\\text{acid}\\pK_a=10}}{H-B} \longrightarrow \underset{\substack{\text{Weaker}\\\text{acid}\\pK_a=20}}{A-H} + \underset{\substack{\text{Weaker}\\\text{base}}}{B:^-}$$

3.33 (a) $C_6H_5-C\equiv C-H + NaNH_2 \xrightarrow[\text{ether}]{} C_6H_5-C\equiv C:^- Na^+ + NH_3$

then

$C_6H_5-C\equiv C:^- Na^+ + T_2O \longrightarrow C_6H_5-C\equiv C-T + NaOT$

(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-H + NaH \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O^- Na^+ + H_2$

then

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O^- Na^+ + D_2O \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-D + NaOD$

(c) $CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2O^- Na^+ + H_2$

then

$CH_3CH_2CH_2O^- Na^+ + D_2O \longrightarrow CH_3CH_2CH_2OD + NaOD$

3.34 (a) $CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

Oxygen is more electronegative than nitrogen, which is more electronegative than carbon. The O-H bond is most polarized, the N-H bond is next, and the C-H bond is least polarized.

(b) $CH_3CH_2O^- < CH_3CH_2\bar{N}H < CH_3CH_2\bar{C}H_2$

The weaker the acid, the stronger the conjugate base.

3.35 (a) $CH_3C{\equiv}CH > CH_3CH{=}CH_2 > CH_3CH_2CH_3$

(b) $CH_3CHClCO_2H > CH_3CH_2CO_2H > CH_3CH_2CH_2OH$

(c) $CH_3CH_2\overset{+}{O}H_2 > CH_3CH_2OH > CH_3OCH_3$

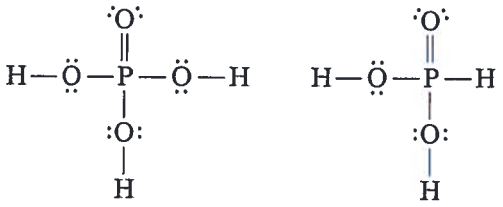
3.36 (a) $CH_3\overset{+}{N}H_3 < CH_3NH_2 < CH_3\bar{N}H$

(b) $CH_3O^- < CH_3\bar{N}H < CH_3\bar{C}H_2$

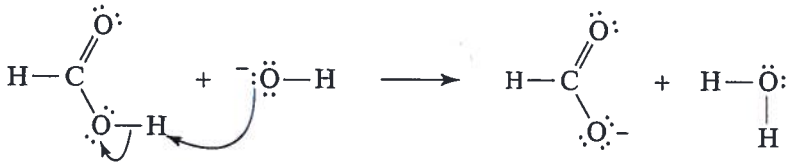
(c) $CH_3C{\equiv}C^- < CH_3CH{=}\bar{C}H < CH_3CH_2\bar{C}H_2$

General Problems

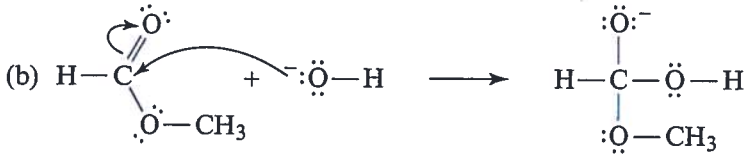
3.37 The acidic hydrogens must be attached to oxygen atoms. In H_3PO_3, one hydrogen is bonded to a phosphorus atom:



3.38 (a)



(b)



(c)

