Chapter 2 – Polar Covalent Bonds; Acids and Bases

Solutions to Problems

2.1 After solving this problem, use Figure 2.3 to check your answers. The larger the number, the more electronegative the element.

More electronegative	*Less electronegative*
(a) H (2.1)	Li (1.0)
(b) Br (2.8)	B (2.0)
(c) Cl (3.0)	I (2.5)
(d) C (2.5)	H (2.1)

Carbon is slightly more electronegative than hydrogen.

2.2 As in Problem 2.1, use Figure 2.3. The partial negative charge is placed on the more electronegative atom, and the partial positive charge is placed on the less electronegative atom.

(a) $H_3C^{\delta+}-Cl^{\delta-}$

(b) $H_3C^{\delta+}-NH_2^{\delta-}$

(c) $H_2N^{\delta-}-H^{\delta+}$

(d) H_3C-SH

Carbon and sulfur have identical electronegativies.

(e) $H_3C^{\delta-}-MgBr^{\delta+}$

(f) $H_3C^{\delta+}-F^{\delta-}$

2.3 Use Figure 2.3 to find the electronegativities of each element. Calculate ΔEN and rank the answers in order of increasing ΔEN.

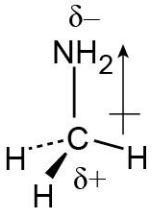
Carbon:	EN = 2.5	Carbon:	EN = 2.5	Fluorine:	EN = 4.0
Lithium:	EN = 1.0	Potassium:	EN = 0.8	Carbon:	EN = 2.5
	ΔEN = 1.5		ΔEN = 1.7		ΔEN = 1.5

Carbon:	EN = 2.5	Oxygen:	EN = 3.5
Magnesium:	EN = 1.2	Carbon:	EN = 2.5
	ΔEN = 1.3		ΔEN = 1.0

The most polar bond has the largest ΔEN. Thus, in order of increasing bond polarity:

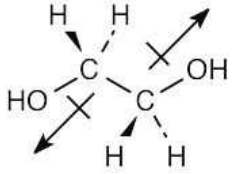
$$H_3C-OH < H_3C-MgBr < H_3C-Li,\ H_3C-F < H_3C-K$$

2.4 In an electrostatic potential map, the color red indicates regions of a molecule that are electron-rich. The map shows that nitrogen is the most electronegative atom in chloromethane, and the direction of polarity of the C–N bond is:



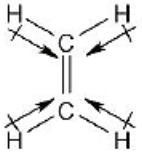
Methylamine

2.5

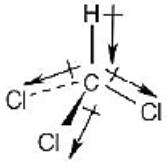
Ethylene glycol 

The dipole moment of ethylene glycol is zero because the bond polarities of the two carbon–oxygen bonds cancel.

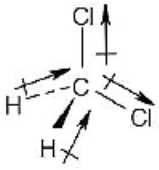
2.6 For each bond, identify the more electronegative element, and draw an arrow that points from the less electronegative element to the more electronegative element. Estimate the sum of the individual dipole moments to arrive at the dipole moment for the entire molecule.

(a) 

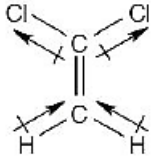
0 dipole moment

(b) 

net dipole moment

(c) 

net dipole moment

(d) 

net dipole moment

2.7 To find the formal charge of an atom in a molecule, follow these two steps:

(1) Draw an electron-dot structure of the molecule.

(2) Use the formula in Section 2.3 (shown below) to determine formal charge for each atom. The periodic table shows the number of valence electrons of the element, and the electron-dot structure shows the number of bonding and nonbonding electrons.

$$\text{Formal charge (FC)} = \begin{bmatrix}\#\text{ of valence}\\ \text{electrons}\end{bmatrix} - \begin{bmatrix}\dfrac{\#\text{ of bonding electrons}}{2}\end{bmatrix} - \begin{bmatrix}\#\text{ nonbonding}\\ \text{electrons}\end{bmatrix}$$

(a)

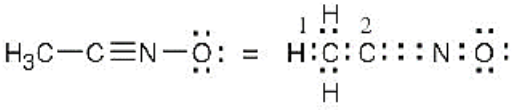
$$\text{For carbon: FC} = 4 - \frac{8}{2} - 0 = 0$$

$$\text{For nitrogen 1: FC} = 5 - \frac{8}{2} - 0 = +1$$

$$\text{For nitrogen 2: FC} = 5 - \frac{4}{2} - 4 = -1$$

Remember: *Valence electrons* are the electrons characteristic of a specific element. *Bonding electrons* are those electrons involved in bonding to other atoms. *Nonbonding electrons* are those electrons in lone pairs.

(b)



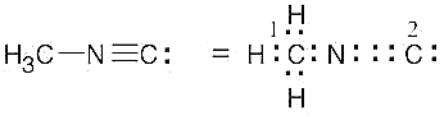
$$\text{For carbon 1: FC} = 4 - \frac{8}{2} - 0 = 0$$

$$\text{For carbon 2: FC} = 4 - \frac{8}{2} - 0 = 0$$

$$\text{For nitrogen : FC} = 5 - \frac{8}{2} - 0 = +1$$

$$\text{For oxygen: FC} = 6 - \frac{2}{2} - 6 = -1$$

(c)



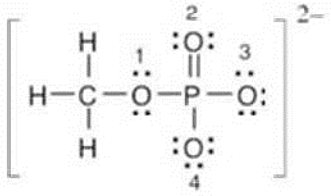
$$\text{For carbon 1: FC} = 4 - \frac{8}{2} - 0 = 0$$

$$\text{For carbon 2: FC} = 4 - \frac{6}{2} - 2 = -1$$

$$\text{For nitrogen : FC} = 5 - \frac{8}{2} - 0 = +1$$

2.8

$$\text{Formal charge (FC)} = \left[\begin{array}{c}\#\text{ of valence}\\ \text{electrons}\end{array}\right] - \left[\frac{\#\text{ of bonding electrons}}{2}\right] - \left[\begin{array}{c}\#\text{ nonbonding}\\ \text{electrons}\end{array}\right]$$



Methyl phosphate

For oxygen 1: $FC = 6 - \frac{4}{2} - 4 = 0$

For oxygen 2: $FC = 6 - \frac{4}{2} - 4 = 0$

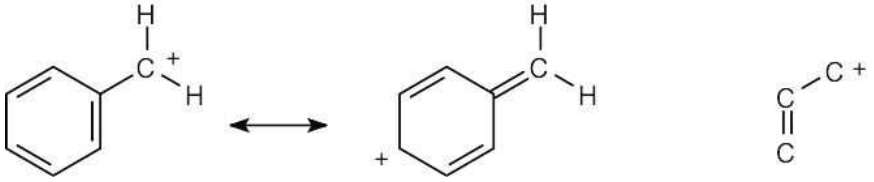
For oxygen 3 : $FC = 6 - \frac{2}{2} - 6 = -1$

For oxygen 4: $FC = 6 - \frac{2}{2} - 6 = -1$

Oxygen atoms 3 and 4 each have a formal charge of –1, and oxygen atoms 1 and 2 have a formal charge of 0.

2.9 Try to locate the three-atom groupings that are present in resonance forms.

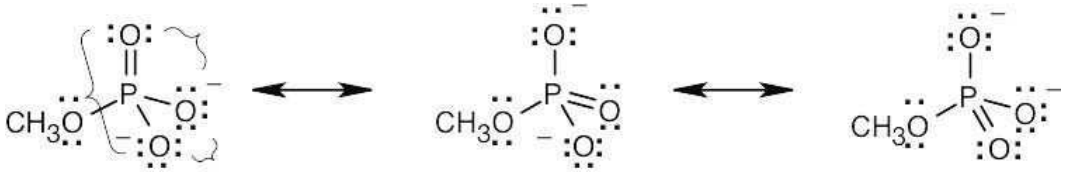
(a) These two structures represent resonance forms. The three-atom grouping (C–C double bond and an adjacent vacant *p* orbital) is pictured on the right.



(b) These two structures represent different compounds, not resonance structures.

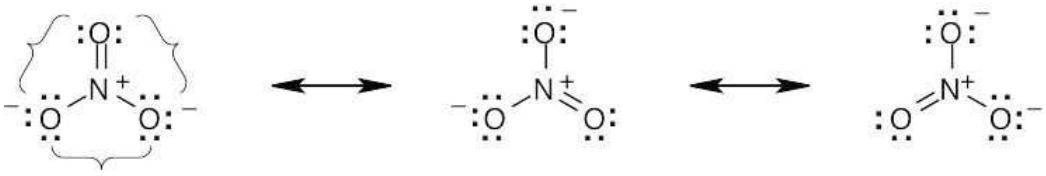
2.10 Look for three-atom groupings that contain a multiple bond next to an atom with a *p* orbital. Exchange the positions of the bond and the electrons in the *p* orbital to draw the resonance form of each grouping.

(a) Methyl phosphate anion has 3 three-atom groupings and thus has 3 resonance forms.

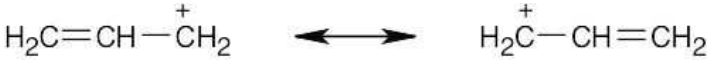


Recall from Chapter 1 that phosphorus, a third-row element, can form more than four covalent bonds

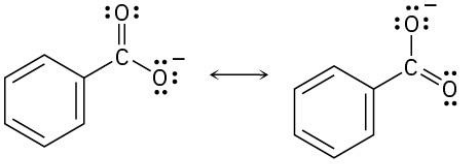
(b)



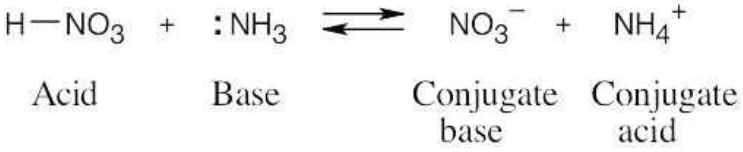
(c)



(d)



2.11 When an acid loses a proton, the product is the conjugate base of the acid. When a base gains a proton, the product is the conjugate acid of the base.

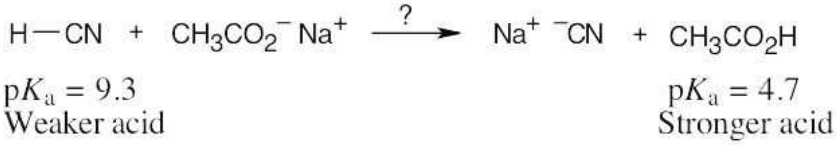


2.12 Recall from Section 2.8 that a stronger acid has a smaller pK_a and a weaker acid has a larger pK_a. Accordingly, phenylalanine (pK_a = 1.83) is a stronger acid than tryptophan (pK_a = 2.83).

2.13 HO–H is a stronger acid than H_2N–H. Since H_2N^- is a stronger base than HO^-, the conjugate acid of H_2N^- (H_2N–H) is a weaker acid than the conjugate acid of HO^- (HO–H).

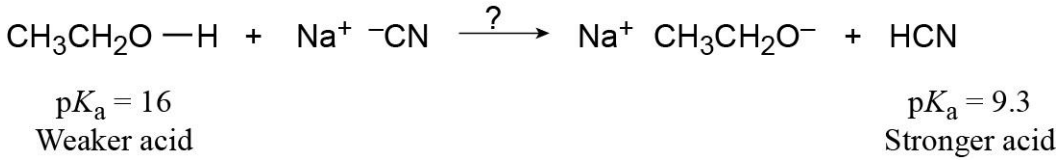
2.14 Use Table 2.3 to find the strength of each acid. A reaction takes place as written if the stronger acid is the reactant.

(a)



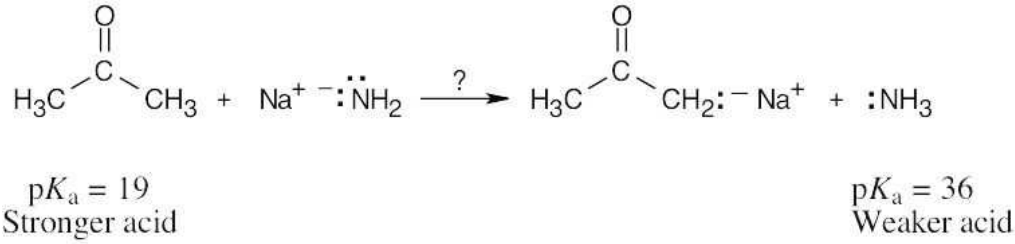
Remember that the lower the pK_a, the stronger the acid. Thus CH_3CO_2H, not HCN, is the stronger acid, and the above reaction will not take place to a significant extent in the direction written.

(b)



Using the same reasoning as in part (a), we can see that the above reaction will not occur to a significant extent.

2.15

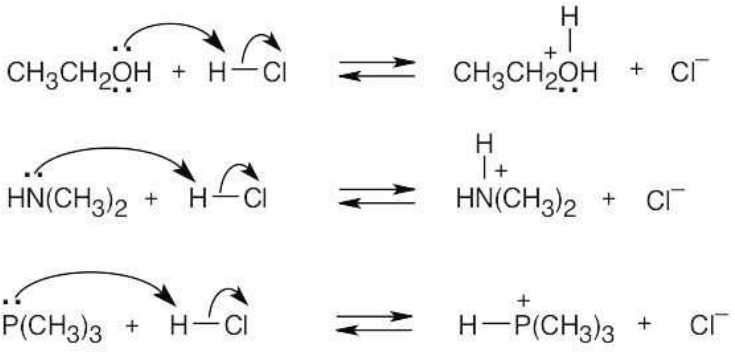


As written, the above reaction will take place to virtual completion due to the large difference in pK_a values.

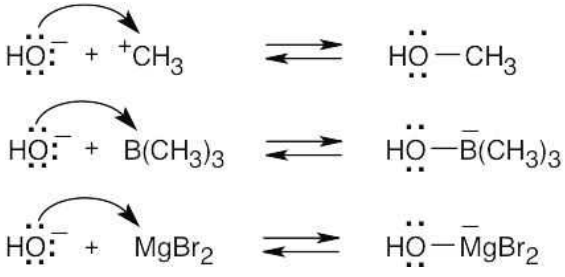
2.16 Enter –9.31 into a calculator and use the INV LOG function to arrive at the answer $K_a = 4.9 \times 10^{-10}$.

2.17 Locate the electron pair(s) of the Lewis base and draw a curved arrow from the electron pair to the Lewis acid. The electron pair moves from the atom at the tail of the arrow (Lewis base) to the atom at the point of the arrow (Lewis acid). (Note: electron dots have been omitted from Cl^- to reduce clutter.)

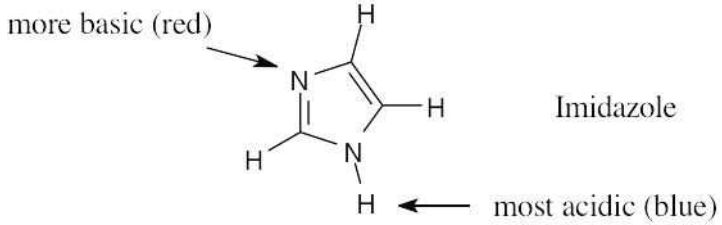
(a)



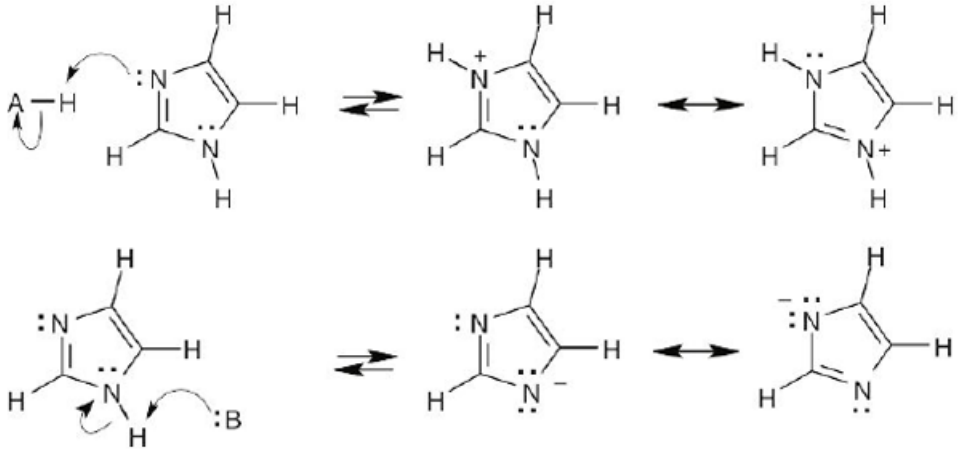
(b)



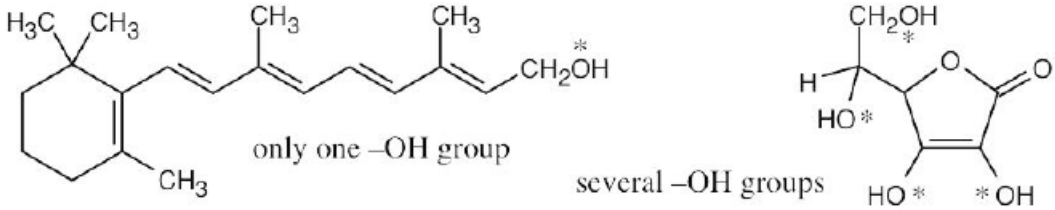
2.18 (a) The nitrogen on the left is more electron-rich and more basic. The indicated hydrogen is most electron-poor (bluest) and is most acidic.



(b)



2.19

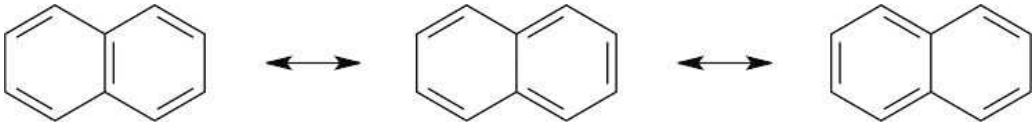


Vitamin C is water-soluble (hydrophilic) because it has several polar –OH groups that can form hydrogen bonds with water. Vitamin A is fat-soluble (hydrophobic) because most of its atoms can't form hydrogen bonds with water.

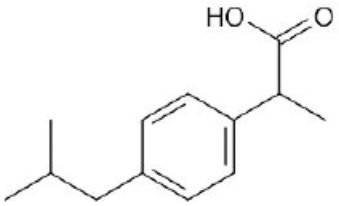
Additional Problems

Visualizing Chemistry

2.20 Naphthalene has three resonance forms.



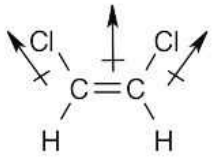
2.21



Ibuprofen

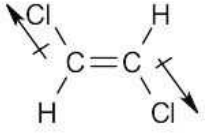
2.22 Electrostatic potential maps show that the electron-rich regions of the cis isomer lie on the same side of the double bond, leading to a net dipole moment. Because the electron-rich regions of the trans isomer are symmetrical about the double bond, the individual bond dipole moments cancel, and the isomer has no overall dipole moment.

net dipole moment



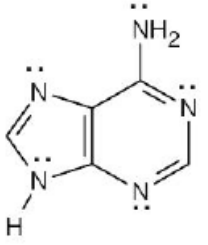
cis-1,2-Dichloroethylene

zero dipole moment



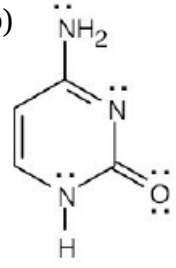
trans-1,2-Dichloroethylene

2.23 (a)



Adenine

(b)

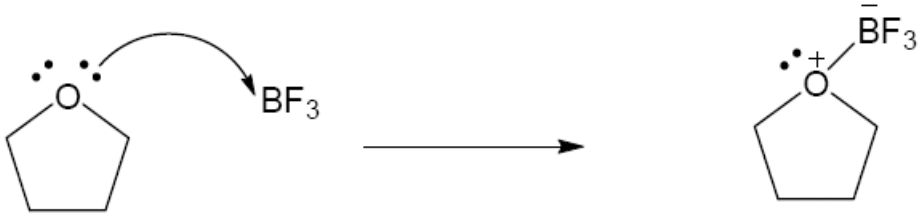


Cytosine

Mechanism Problems

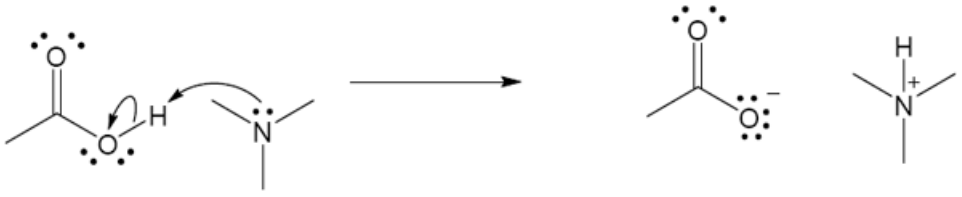
2.24

(a)



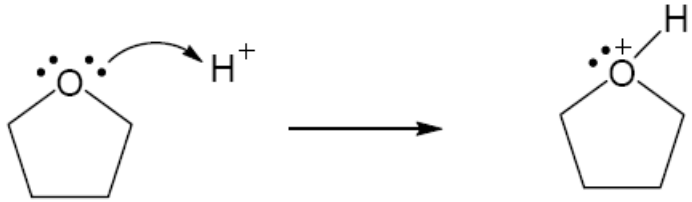
(b)

(c)

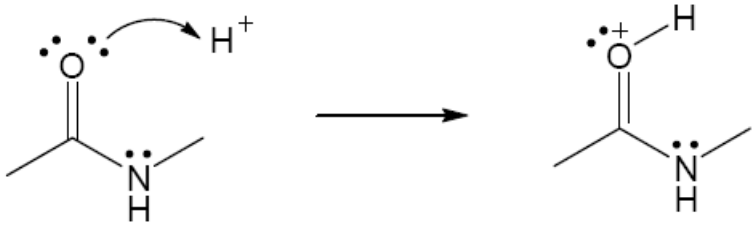


2.25

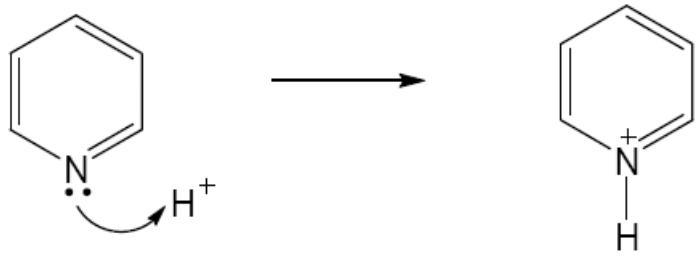
(a)



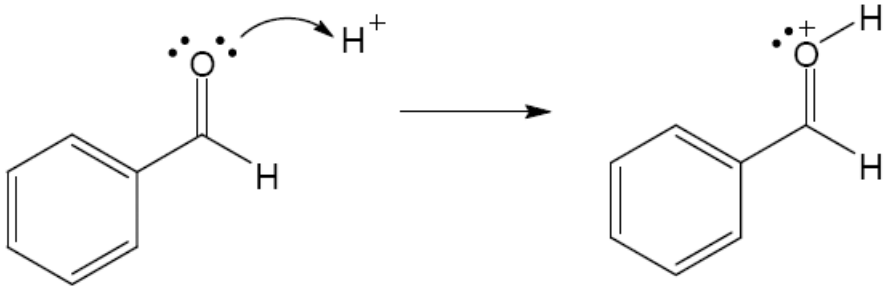
(b)



(c)

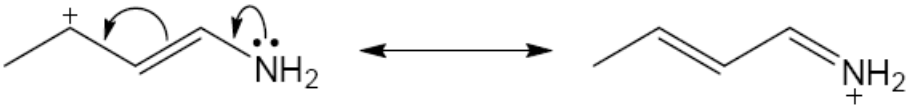


(d)

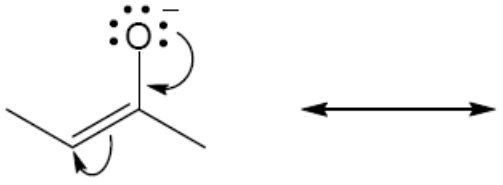


2.26

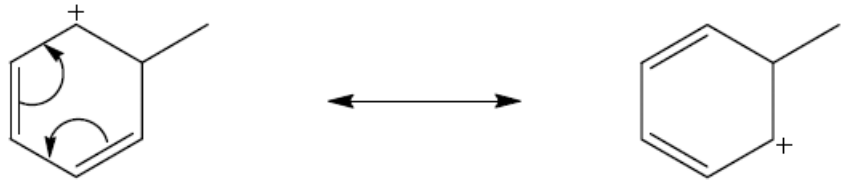
(a)



(b)

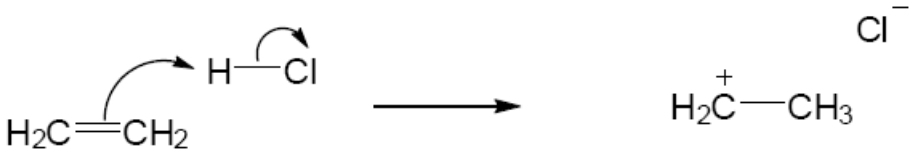


(c)



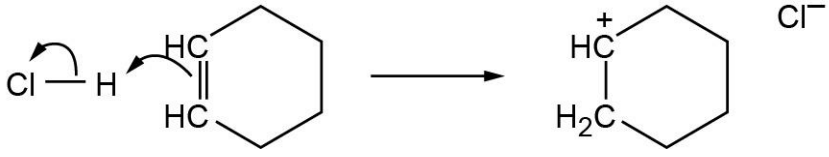
2.27

(a)



(b)

(c)

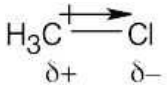
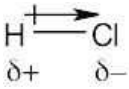
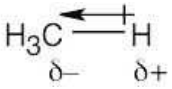
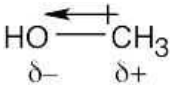
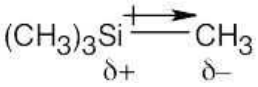
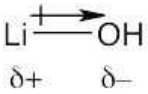
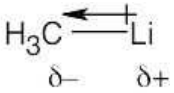


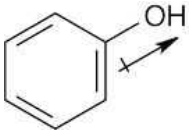
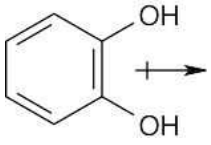
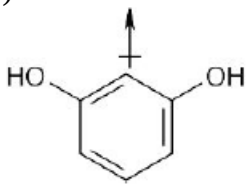
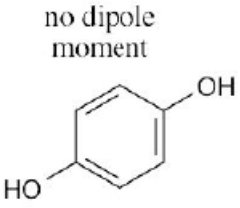
Electronegativity and Dipole Moments

2.28 Use Figure 2.3 if you need help. The most electronegative element is starred.

(a) $CH_2\overset{*}{F}Cl$ (b) $\overset{*}{F}CH_2CH_2CH_2Br$ (c) $H\overset{*}{O}CH_2CH_2NH_2$ (d) $CH_3\overset{*}{O}CH_2Li$

2.29

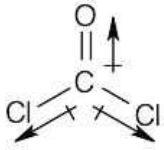
	More polar	*Less polar*
(a)		
(b)		
(c)		
(d)		

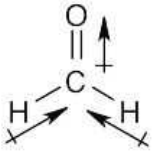
2.30 (a)  (b)  (c)  (d) 

2.31 (a) In Section 2.2, we found that $\mu = Q \times r$. If the two charges are separated by 136 pm, μ = 6.53 D.

(b) Since the observed dipole moment is 1.08 D, the H–Cl bond has (1.08 D / 6.53 D) × 100 % = 16.5 % ionic character.

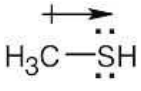
2.32 In phosgene, the individual bond polarities tend to cancel, but in formaldehyde, the bond polarities add to each other. Thus, phosgene has a smaller dipole moment than formaldehyde.


Phosgene


Formaldehyde

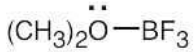
2.33 The magnitude of a dipole moment depends on both charge and distance between atoms. Fluorine is more electronegative than chlorine, but a C–F bond is shorter than a C–Cl bond. Thus, the dipole moment of CH_3F is smaller than that of CH_3Cl.

2.34 The observed dipole moment is due to the lone pair of electrons on sulfur.



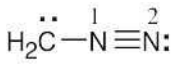
Formal Charges

2.35 To save space, molecules are shown as line-bond structures with lone pairs, rather than as electron-dot structures.

(a) 

$$\text{Oxygen: FC} = 6 - \frac{6}{2} - 2 = +1$$

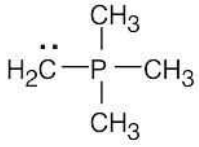
$$\text{Boron: FC} = 3 - \frac{8}{2} - 0 = -1$$

(b) 

$$\text{Carbon: FC} = 4 - \frac{6}{2} - 2 = -1$$

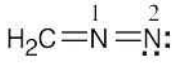
$$\text{Nitrogen 1: FC} = 5 - \frac{8}{2} - 0 = +1$$

$$\text{Nitrogen 2: FC} = 5 - \frac{6}{2} - 2 = 0$$

(c) 

$$\text{Carbon: FC} = 4 - \frac{6}{2} - 2 = -1$$

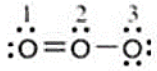
$$\text{Phosphorus: FC} = 5 - \frac{8}{2} - 0 = +1$$

(d) 

$$\text{Carbon: FC} = 4 - \frac{8}{2} - 0 = 0$$

$$\text{Nitrogen 1: FC} = 5 - \frac{8}{2} - 0 = +1$$

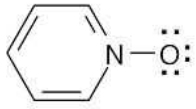
$$\text{Nitrogen 2: FC} = 5 - \frac{4}{2} - 4 = -1$$

(e) 

$$\text{Oxygen 1: FC} = 6 - \frac{4}{2} - 4 = 0$$

$$\text{Oxygen 2: FC} = 6 - \frac{6}{2} - 2 = +1$$

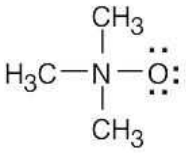
$$\text{Oxygen 3: FC} = 6 - \frac{2}{2} - 6 = -1$$

(f) 

$$\text{Nitrogen: FC} = 5 - \frac{8}{2} - 0 = +1$$

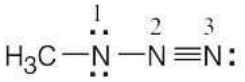
$$\text{Oxygen: FC} = 6 - \frac{2}{2} - 6 = -1$$

2.36 As in Problem 2.31, molecules are shown as line-bond structures with lone-pair electrons indicated. Only calculations for atoms with non-zero formal charge are shown.

(a) 

$$\text{Oxygen: FC} = 6 - \frac{2}{2} - 6 = -1$$

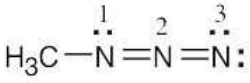
$$\text{Nitrogen: FC} = 5 - \frac{8}{2} - 0 = +1$$

(b) 

$$\text{Nitrogen 1: FC} = 5 - \frac{4}{2} - 4 = -1$$

$$\text{Nitrogen 2: FC} = 5 - \frac{8}{2} - 0 = +1$$

$$\text{Nitrogen 3: FC} = 5 - \frac{6}{2} - 2 = 0$$

(c) 

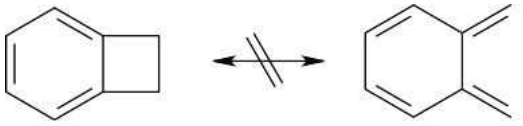
$$\text{Nitrogen 1: FC} = 5 - \frac{6}{2} - 2 = 0$$

$$\text{Nitrogen 2: FC} = 5 - \frac{8}{2} - 0 = +1$$

$$\text{Nitrogen 3: FC} = 5 - \frac{4}{2} - 4 = -1$$

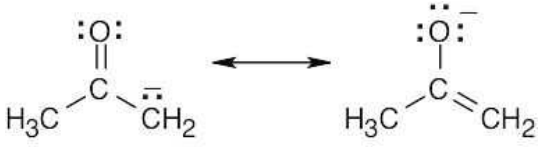
Resonance

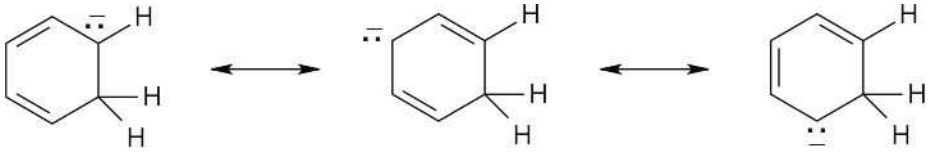
2.37 Resonance forms do not differ in the position of nuclei. The two structures in (a) are not resonance forms because the positions of the carbon and hydrogen atoms outside the ring are different in the two forms.

 not resonance structures

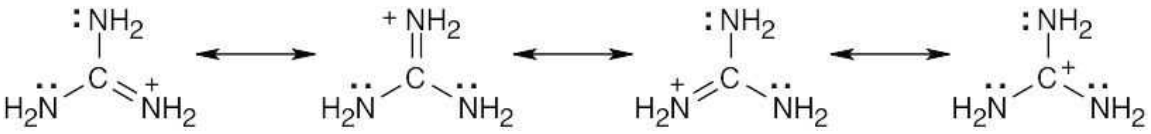
The pairs of structures in parts (b), (c), and (d) represent resonance forms.

2.38

(a) 

(b) 

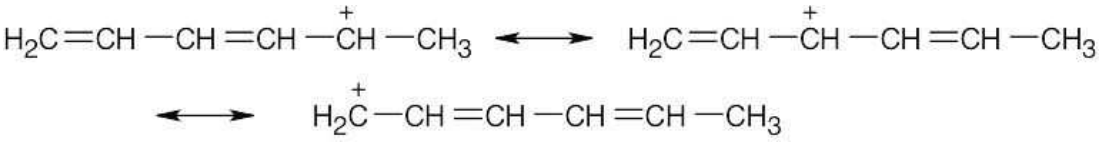
(c)



The last resonance structure is a minor contributor because its carbon lacks a complete electron octet.

(d)

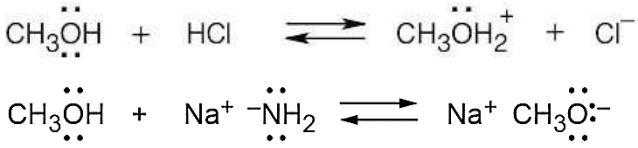
(e)



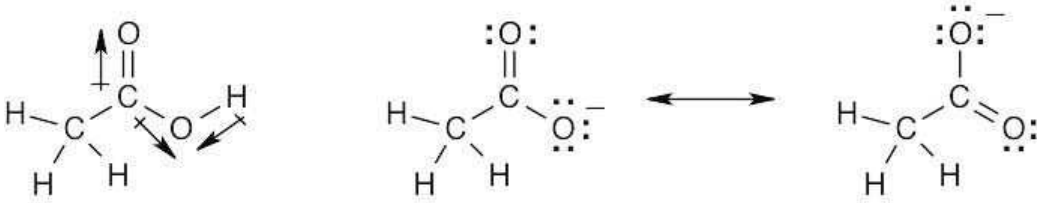
2.39 The two structures are not resonance forms because the positions of the carbon atoms are different in the two forms.

Acids and Bases

2.40



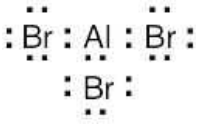
2.41



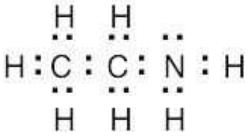
The O–H hydrogen of acetic acid is more acidic than the C–H hydrogens. The –OH oxygen is electronegative, and, consequently, the –O–H bond is more strongly polarized than the –C–H bonds. In addition, the acetate anion is stabilized by resonance.

2.42

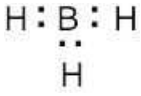
(a)



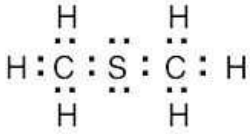
(b)

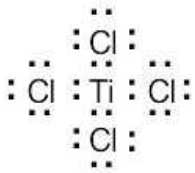


(c)



(d)

(e) 

(f) 

The Lewis acids shown below can accept an electron pair either because they have a vacant orbital or because they can donate H^+. The Lewis bases have nonbonding electron pairs.

Lewis acids: $AlBr_3$, BH_3, HF, $TiCl_4$

Lewis bases: $CH_3CH_2\ddot{N}H_2$, $H_3C-\ddot{S}-CH_3$

2.43

(a) $CH_3OH + H_2SO_4 \rightleftharpoons CH_3OH_2^+ + HSO_4^-$

stronger base; stronger acid; weaker acid; weaker base

(b) $CH_3OH + NaNH_2 \rightleftharpoons CH_3O^-\,Na^+ + NH_3$

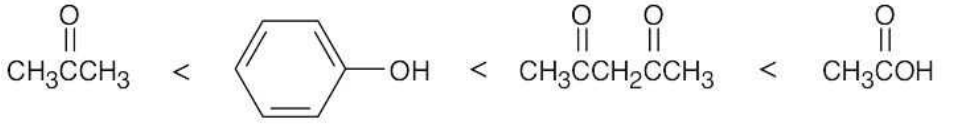
stronger acid; stronger base; weaker base; weaker acid

(c) $CH_3NH_3^+\,Cl^- + NaOH \rightleftharpoons CH_3NH_2 + H_2O + NaCl$

stronger acid; stronger base; weaker base; weaker acid

2.44 The substances with the largest values of pK_a are the least acidic.

Least acidic ⟶ *Most acidic*



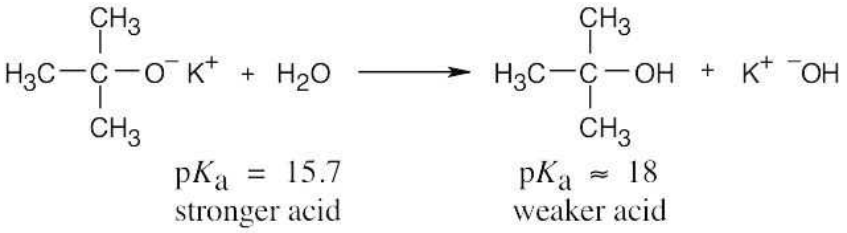
CH_3CCH_3 < < $CH_3CCH_2CCH_3$ < CH_3COH

pK_a = 19.3 pK_a = 9.9 pK_a = 9 pK_a = 4.76

2.45 To react completely (> 99.9%) with NaOH, an acid must have a pK_a at least 3 units smaller than the pK_a of H_2O. Thus, all substances in the previous problem except acetone react completely with NaOH.

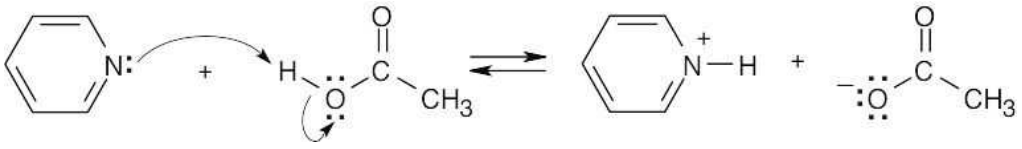
2.46 The stronger the acid (smaller pK_a), the weaker its conjugate base. Since NH_4^+ is a stronger acid than $CH_3NH_3^+$, CH_3NH_2 is a stronger base than NH_3.

2.47



The reaction takes place as written because water is a stronger acid than *tert*-butyl alcohol. Thus, a solution of potassium *tert*-butoxide in water can't be prepared.

2.48



2.49 (a) Acetone: $K_a = 5 \times 10^{-20}$ (b) Formic acid: $K_a = 1.8 \times 10^{-4}$

2.50 (a) Nitromethane: $pK_a = 10.30$ (b) Acrylic acid: $pK_a = 4.25$

2.51

$$\underset{[0.050\ M]}{\text{Formic acid}} + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} \underset{[x]}{\text{Formate}} + \underset{[x]}{H_3O^+}$$

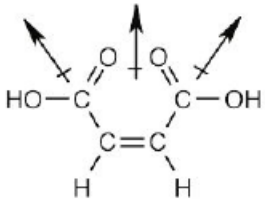
$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

If you let $0.050 - x = 0.050$, then $x = 3.0 \times 10^{-3}$ and pH = 2.52. If you calculate x exactly using the quadratic equation, then $x = 2.9 \times 10^{-3}$ and pH = 2.54.

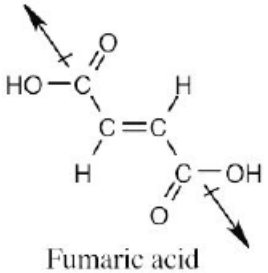
2.52 Only acetic acid will react with sodium bicarbonate. Acetic acid is the only substance in Problem 2.40 that is a stronger acid than carbonic acid.

General Problems

2.53 In maleic acid, the individual dipole moments add to produce a net dipole moment for the whole molecule. The individual dipole moments in fumaric acid cancel, resulting in a zero dipole moment.



Maleic acid

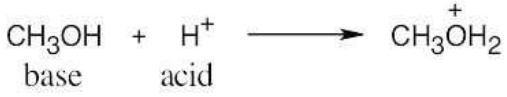


Fumaric acid

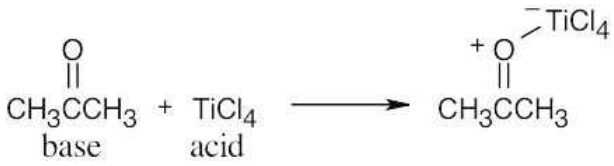
2.54 Sodium bicarbonate reacts with acetic acid to produce carbonic acid, which breaks down to form CO_2. Thus, bubbles of CO_2 indicate the presence of an acid stronger than carbonic acid, in this case acetic acid, as the pK_a values indicate. Phenol does not react with sodium bicarbonate.

2.55 Reactions (a) and (c) are reactions between Brønsted–Lowry acids and bases; the stronger acid and stronger base are identified. Reactions (b) and (d) occur between Lewis acids and bases.

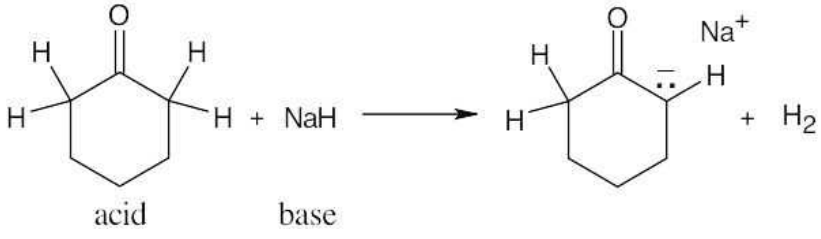
(a)



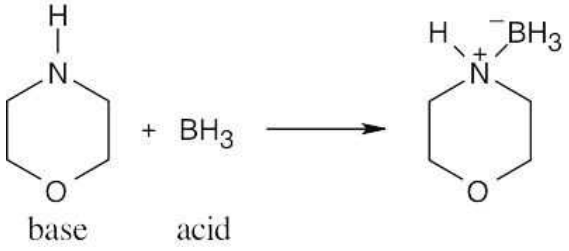
(b)



(c)



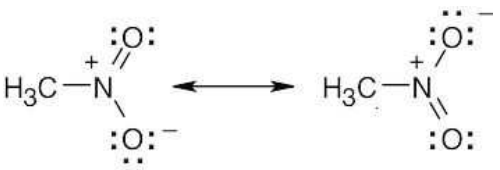
(d)



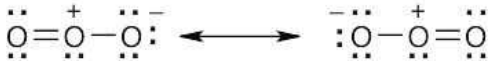
2.56 Pairs (a) and (d) represent resonance structures; pairs (b) and (c) do not. For two structures to be resonance forms, all atoms must be in the same positions in all resonance forms.

2.57

(a)

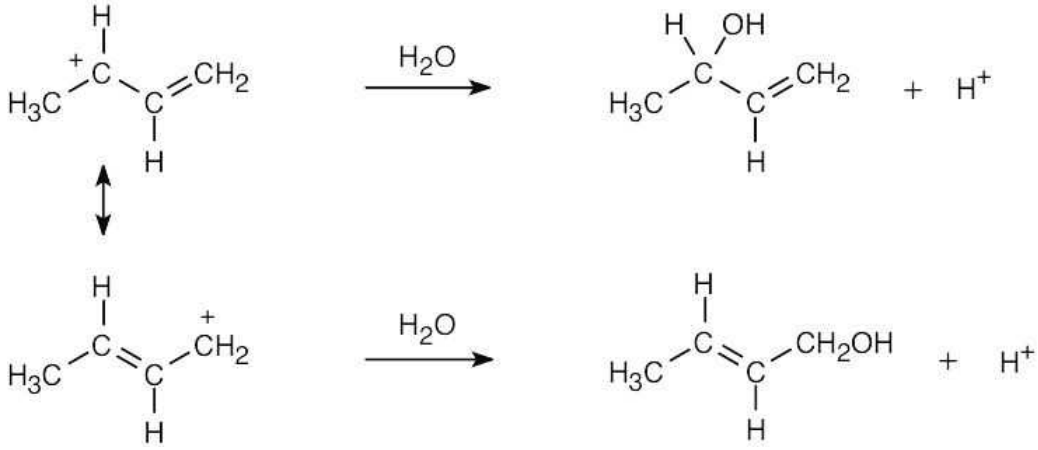


(b)



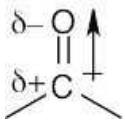
(c)

2.58 The cation can be represented by two resonance forms. Reaction with water can occur at either positively charged carbon, resulting in two products.

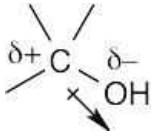


2.59

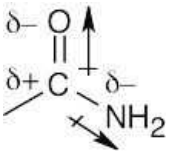
(a)



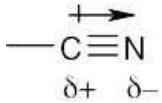
(b)



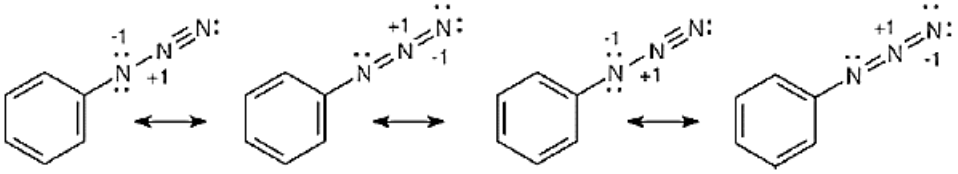
(c)



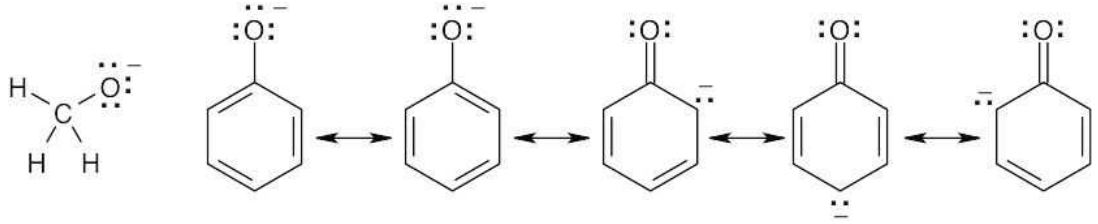
(d)



2.60

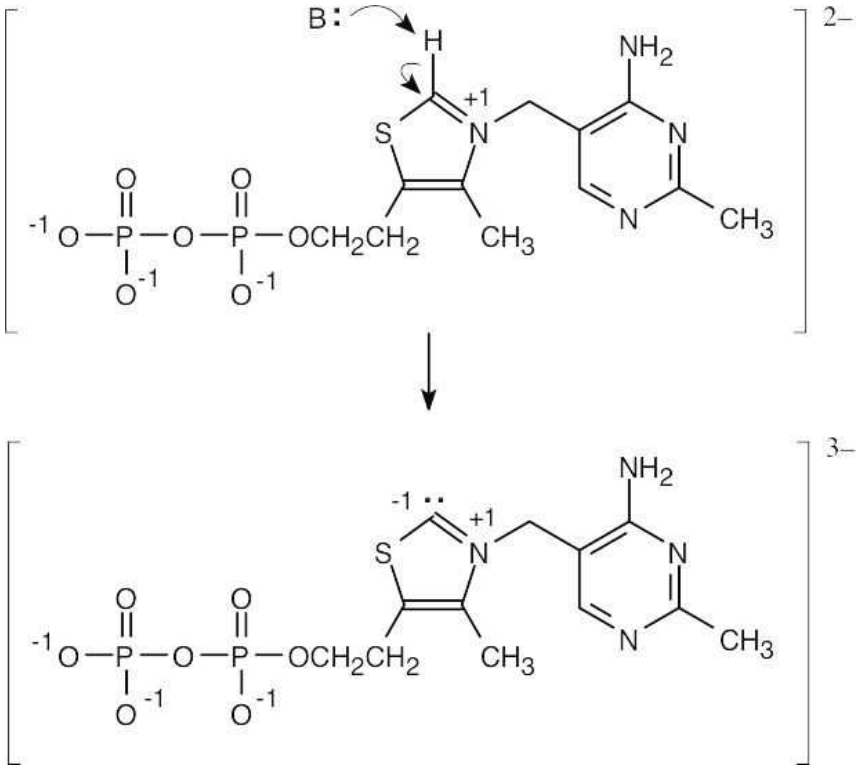


2.61

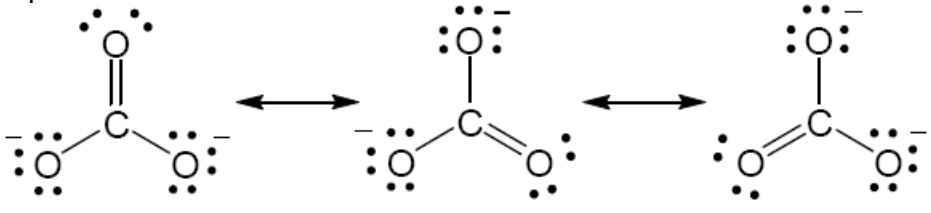


When phenol loses a proton, the resulting anion is stabilized by resonance. The methanol anion is not stabilized by resonance.

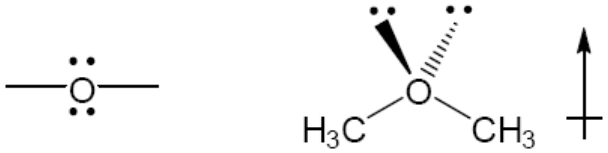
2.62



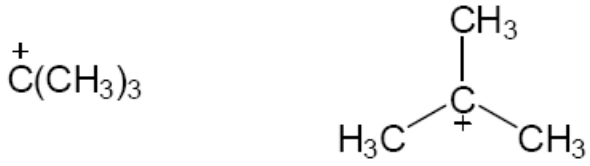
2.63 (a) The central carbon of carbonate ion is sp^2 and trigonal planar. The three resonance forms contribute equally to the overall resonance hybrid. Thus, the molecule has no dipole.



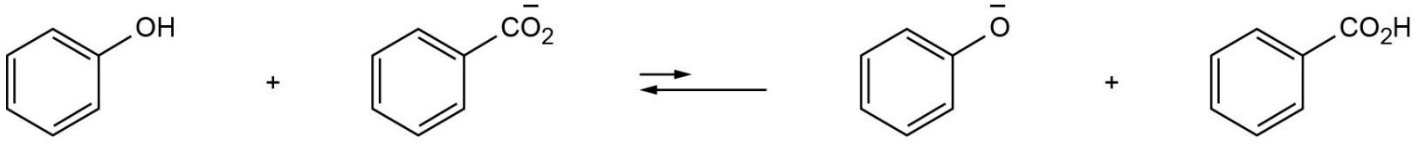
(b) The oxygen is sp^3 hybridized and tetrahedral. Therefore, there is a dipole pointing towards the lone pairs.



(c) The carbocation is sp^2 hybridized and trigonal planar. Thus, there is no dipole.

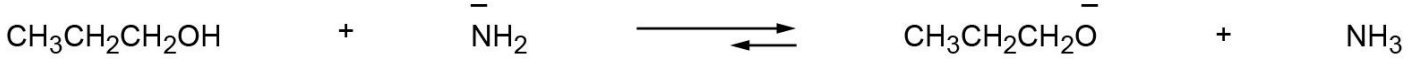


2.64 The equilibrium always favors the weaker acid/base pair (acid with the higher pK_a). (a)



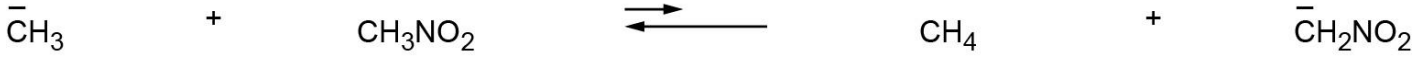
pK_a 9.9 pK_a 4.2

(b)



pK_a 16.1 pK_a 36

(c)



pK_a 10.3 pK_a 60

2.65 (a) London dispersion forces

(b) Hydrogen bonding

(c) Hydrogen bonding causes the carboxylic acids to interact with one another and that force is stronger than the dispersion forces between acetic acid and oil.

This file is copyright 2023, Rice University. All Rights Reserved.