

Solutions Manual

Jan William Simek

California Polytechnic State University

ORGANIC CHEMISTRY

EIGHTH EDITION

L. G. WADE, JR.

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PREFACE

Hints for Passing Organic Chemistry

Do you want to pass your course in organic chemistry? Here is my best advice, based on over thirty-five years of observing students learning organic chemistry:

Hint #1: *Do the problems.* It seems straightforward, but humans, including students, try to take the easy way out until they discover there is no shortcut. Unless you have a measured IQ above 200 and comfortably cruise in the top 1% of your class, *do the problems.* Usually your teacher (professor or teaching assistant) will recommend certain ones; try to do all those recommended. If you do half of them, you will be half-prepared at test time. (Do you want your surgeon coming to your appendectomy having practiced only *half* the procedure?) And when you do the problems, keep this Solutions Manual CLOSED. Avoid looking at *my* answer before you write *your* answer—your trying and struggling with the problem is the most valuable part of the problem. Discovery is a major part of learning. Remember that the primary goal of doing these problems is *not* just getting the right answer, but understanding the material well enough to get right answers to the questions you haven't seen yet.

Hint #2: *Keep up.* Getting behind in your work in a course that moves as quickly as this one is the Kiss of Death. For most students, organic chemistry is the most rigorous intellectual challenge they have faced so far in their studies. Some are taken by surprise at the diligence it requires. Don't think that you can study all of the material in the couple of days before the exam—well, you can, but you won't get a passing grade. Study organic chemistry like a foreign language: try to do some every day so that the freshly trained neurons stay sharp.

Hint #3: *Get help when you need it.* Use your teacher's office hours when you have difficulty. Many schools have tutoring centers (in which organic chemistry is a popular offering). Here's a secret: absolutely the best way to cement this material in your brain is to get together with a few of your fellow students and make up problems for each other, then correct and discuss them. When *you* write the problems, you will gain great insight into what this is all about.

Hint #3.5: When you write answers to problem, *write* them. Use the old-fashioned method of a writing implement on paper. Keep a notebook with your work. Show your instructor; he/she will be impressed.

Purpose of This Solutions Manual

So what is the point of this Solutions Manual? First, I can't do your studying for you. Second, since I am not leaning over your shoulder as you write your answers, I can't give you direct feedback on what you write and think—the print medium is limited in its usefulness. What I *can* do for you is: 1) provide correct answers: the publishers, Professor Wade, Professor Palandoken (my reviewer), and I have gone to great lengths to assure that what I have written is correct, for we all understand how it can shake a student's confidence to discover that the answer book flubbed up; 2) provide a considerable degree of rigor: beyond the fundamental requirement of correctness, I have tried to flesh out these answers, being complete but succinct; 3) provide insight into how to solve a problem and into where the sticky intellectual points are. Insight is the toughest to accomplish, but over the years, I have come to understand where students have trouble, so I have tried to anticipate your questions and to add enough detail so that the concept, as well as the answer, is clear.

It is difficult for students to understand or acknowledge that their teachers are human (some are more human than others). Since I am human (despite what my students might report), I can and do make mistakes. If there are mistakes in this book, they are my sole responsibility, and I am sorry. If you find one, PLEASE let me know so that it can be corrected in future printings. Nip it in the bud.

What's New in This edition?

Better answers! Part of my goal in this edition has been to add more explanatory material to clarify how to arrive at the answer. In many problems, the possibility of more than one answer to a problem has been noted. Concept maps have been added at appropriate places to demonstrate the logic of particular concepts.

Better graphics! The print medium is very limited in its ability to convey three-dimensional structural information, a problem that has plagued organic chemists for over a century.

Appendix 2 on Acidity has been revised, and Appendix 3 has been added as a suggestion to students on how to organize reaction summaries to make studying more effective.

Better jokes? Too much to hope for.

Some Web Stuff

Here I am: <http://www.calpoly.edu/~chem/faculty/simek.html> .

The Publisher (Pearson) maintains a web site related to the Wade text: try

<http://www.masteringchemistry.com>

Two essential web sites providing spectra are listed on the bottom of p. 276.

Acknowledgments

No project of this scope is ever done alone. These are team efforts, and several people who have assisted and facilitated in one fashion or another deserve my thanks.

Professor L. G. Wade, Jr., your textbook author, is a remarkable person. He has gone to extraordinary lengths to make the textbook as clear, organized, informative, and insightful as possible. He has solicited and followed many suggestions on his text, and his comments on my solutions have been perceptive and valuable. We agreed early on that our primary goal is to help the students learn a fascinating and challenging subject, and all of our efforts have been directed toward that goal. I have appreciated our collaboration.

My friend and colleague, Dr. Hasan Palandoken, has reviewed the entire manuscript for accuracy and style. His extraordinary diligence, attention to detail, and chemical wisdom have made this a better manual. Hasan stands on the shoulders of previous reviewers who scoured earlier editions for errors: Dr. Kristen Meisenheimer, Jessica Gilman Ernakovich, Dr. Eric Kantorowski, and Dr. Dan Mattern. Mr. Richard King of Pasadena, Texas, Editorial Adviser, has offered numerous suggestions on how to clarify murky explanations. I am grateful to them all.

The people at Pearson have made this project possible. Good books would not exist without their dedication, professionalism, and experience. Among the many people who contributed are: Lee Englander, who originally connected me with this project; Jeanne Zalesky, Executive Editor in Chemistry; Jennifer Hart, Senior Project Editor in Chemistry; and Coleen McDonald, Assistant Editor in Chemistry.

The entire manuscript was produced using *ChemDraw*®, the remarkable software for drawing chemical structures developed by CambridgeSoft Corp., Cambridge, MA.

Finally, I appreciate my friends who supported me throughout this project, most notably my wife and friend of over forty-six years, Judy Lang. The students are too numerous to list, but it is for them that all this happens.

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DEDICATION

To my inspirational chemistry teachers:

Joe Plaskas, who made the batter;
Kurt Kaufman, who baked the cake;
Carl Djerassi, who put on the icing;



and to my parents:

Ervin J. and Imilda B. Simek,
who had the original concept.






SYMBOLS AND ABBREVIATIONS

Below is a list of symbols and abbreviations used in this Solutions Manual, consistent with those used in the textbook by Wade; see the inside front cover of the text. (Do not expect all of these to make sense to you now. You will learn them throughout your study of organic chemistry.)

BONDS

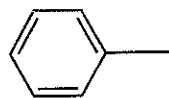
- a single bond
- == a double bond
- ≡ a triple bond
-  a bond in three dimensions, coming out of the paper toward the reader
-  a bond in three dimensions, going behind the paper away from the reader
- a stretched bond, in the process of forming or breaking

ARROWS

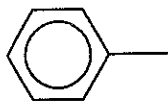
-  in a reaction, shows direction from reactants to products
-  signifies equilibrium (not to be confused with resonance)
-  signifies resonance (not to be confused with equilibrium)
-  shows direction of electron movement:
the arrowhead with one barb shows movement of one electron;
the arrowhead with two barbs shows movement of a pair of electrons
-  shows polarity of a bond or molecule, the arrowhead signifying the more negative end of the dipole

SUBSTITUENT GROUPS

- Me a methyl group, CH_3
- Et an ethyl group, CH_2CH_3
- Pr a propyl group, a three-carbon group (two possible arrangements)
- Bu a butyl group, a four-carbon group (four possible arrangements)
- R the general abbreviation for an alkyl group (or any substituent group bonded at carbon)
- Ph a phenyl group, the name of a benzene ring as a substituent, represented:



or



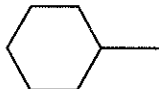
- Ar the general abbreviation for an aromatic group

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Symbols and Abbreviations, continued

SUBSTITUENT GROUPS, continued

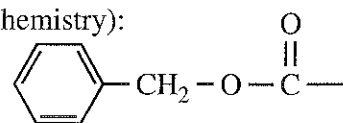
Ac an acetyl group: $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$

c-Hx a cyclohexyl group: 

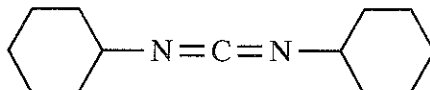
Ts tosyl, or *p*-toluenesulfonyl group: $\text{CH}_3-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{S}}-$

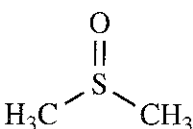
Boc a *tert*-butoxycarbonyl group (amino acid and peptide chemistry): $(\text{CH}_3)_3\text{C}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$

Z, or Cbz a carbobenzoxy (benzyloxycarbonyl) group (amino acid and peptide chemistry):



REAGENTS AND SOLVENTS

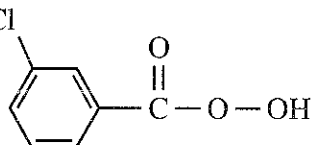
DCC dicyclohexylcarbodiimide 

DMSO dimethylsulfoxide 

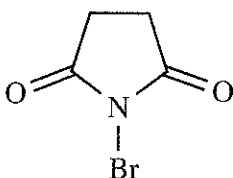
ether diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

HA or H-A is a generic acid; the conjugate base may appear as: A^- A^{\ominus} $:\text{A}^{\ominus}$

LG leaving group

MCPBA *meta*-chloroperoxybenzoic acid 

MVK methyl vinyl ketone 

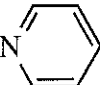
NBS *N*-bromosuccinimide 

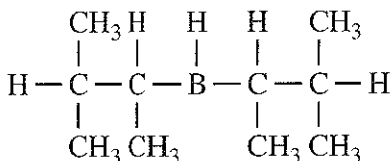
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Symbols and Abbreviations, continued

REAGENTS AND SOLVENTS, continued

Nuc or :Nuc or Nuc⁻ is a generic nucleophile, a Lewis base; E or E⁺ is a generic electrophile, a Lewis acid

PCC pyridinium chlorochromate, CrO₃ • HCl • N 

Sia₂BH disiamylborane 

THF tetrahydrofuran 

SPECTROSCOPY

IR infrared spectroscopy

NMR nuclear magnetic resonance spectroscopy

MS mass spectrometry

UV ultraviolet spectroscopy

ppm parts per million, a unit used in NMR

Hz hertz, cycles per second, a unit of frequency

MHz megahertz, millions of cycles per second

TMS tetramethylsilane, (CH₃)₄Si, the reference compound in NMR

s, d, t, q, m singlet, doublet, triplet, quartet, multiplet: the number of peaks an NMR absorption gives

nm nanometers, 10⁻⁹ meters (usually used as a unit of wavelength)

m/z mass-to-charge ratio, in mass spectrometry

δ in NMR, chemical shift value, measured in ppm (Greek lower case delta)

λ wavelength (Greek lambda)

ν frequency (Greek nu)

J coupling constant in NMR

OTHER

•• or : unshared electron pair

a, ax axial (in chair forms of cyclohexane)

e, eq equatorial (in chair forms of cyclohexane)

HOMO highest occupied molecular orbital

LUMO lowest unoccupied molecular orbital

NR no reaction

o, m, p ortho, meta, para (positions on an aromatic ring)

Δ when written over an arrow: "heat"; when written before a letter: "change in"

δ⁺, δ⁻ partial positive charge, partial negative charge

hν energy from electromagnetic radiation (light)

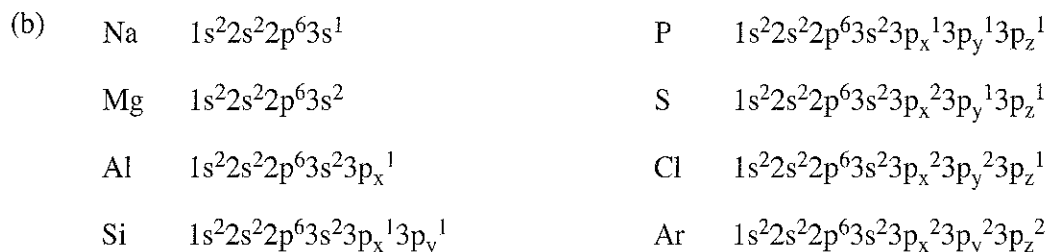
[α]_D specific rotation at the D line of sodium (589 nm)

Students: Add your own notes on symbols and abbreviations.

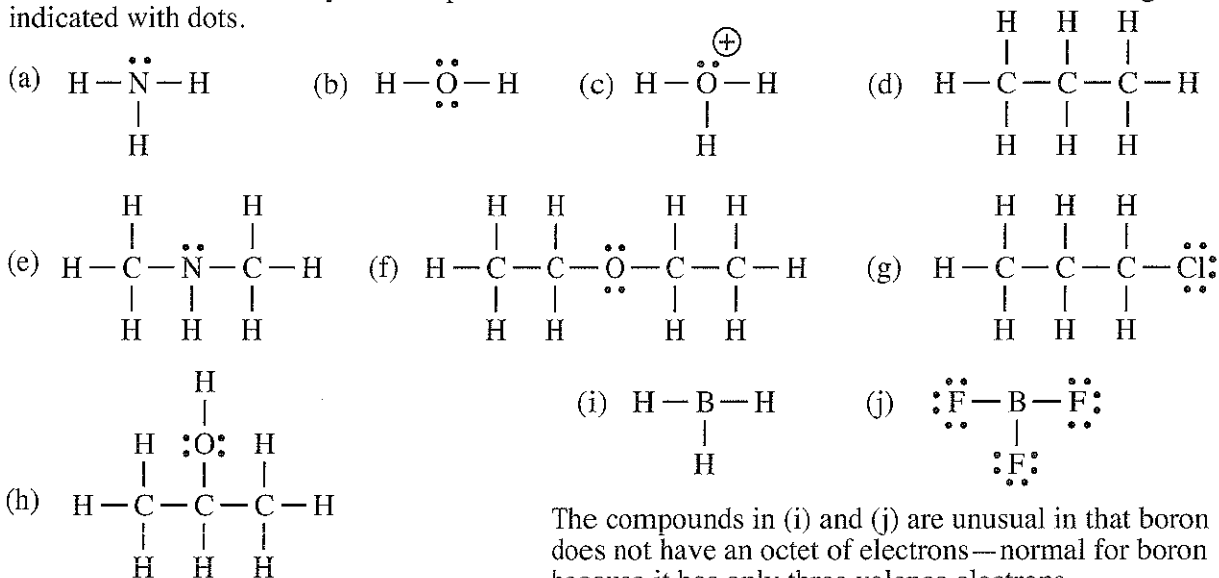
CHAPTER 1—INTRODUCTION AND REVIEW

1-1

(a) Nitrogen has atomic number 7, so all nitrogen atoms have 7 protons. The mass number is the total number of neutrons and protons; therefore, ^{13}N has 6 neutrons, ^{14}N has 7 neutrons, ^{15}N has 8 neutrons, ^{16}N has 9 neutrons, and ^{17}N has 10 neutrons.

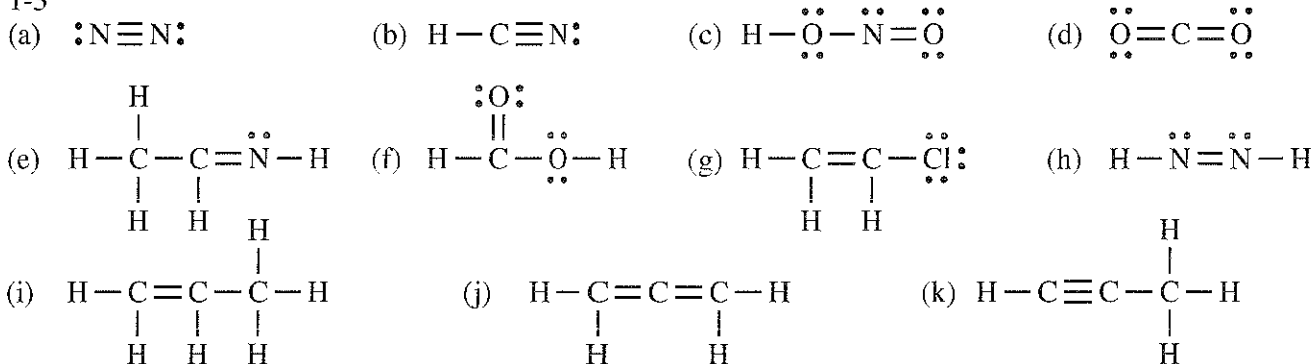


1-2 Lines between atom symbols represent covalent bonds between those atoms. Nonbonding electrons are indicated with dots.

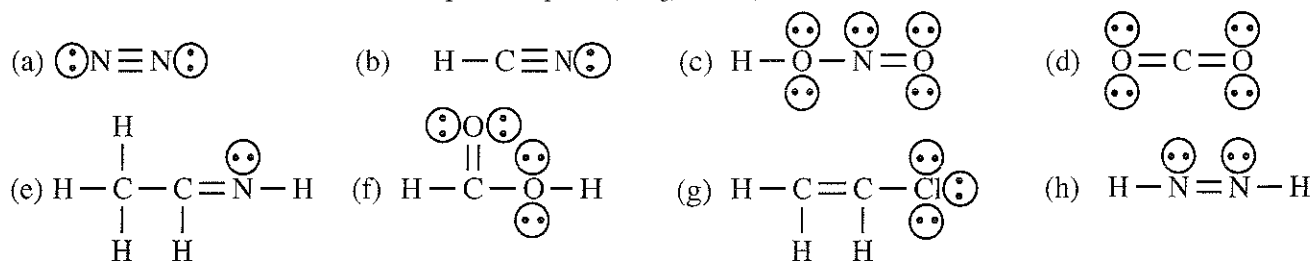


The compounds in (i) and (j) are unusual in that boron does not have an octet of electrons—normal for boron because it has only three valence electrons.

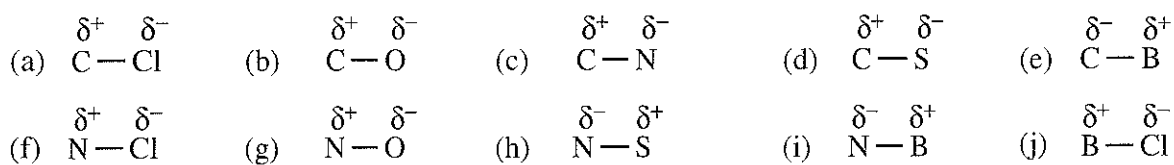
1-3



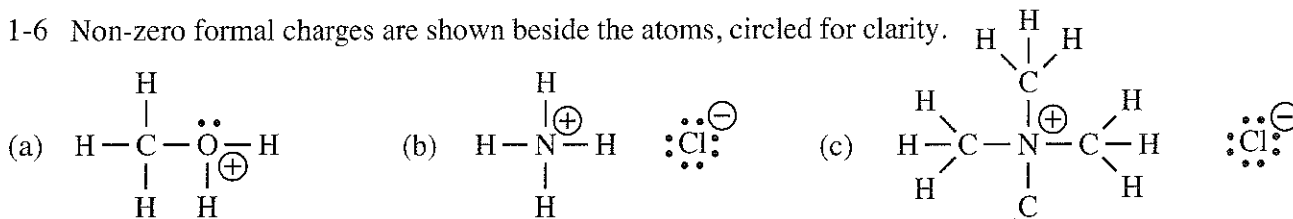
1-4 There are no unshared electron pairs in parts (i), (j), and (k).



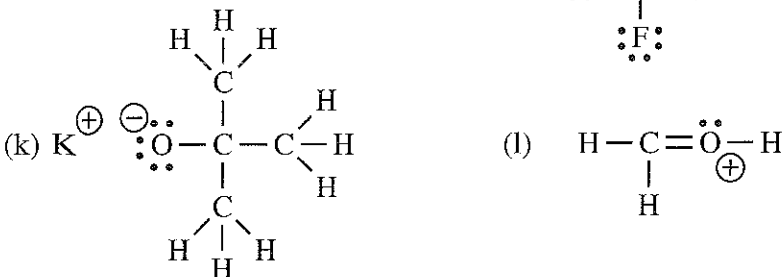
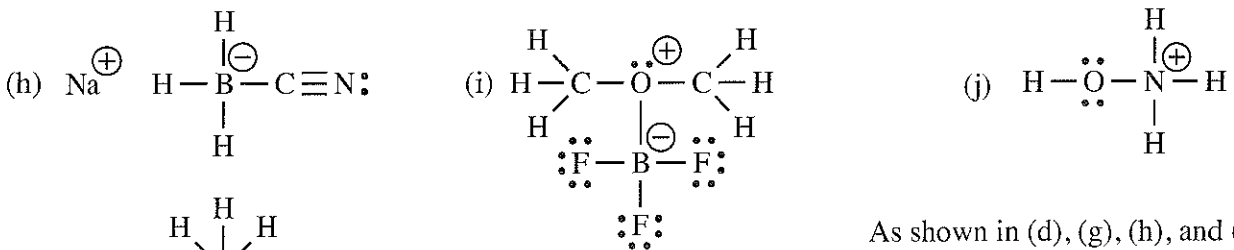
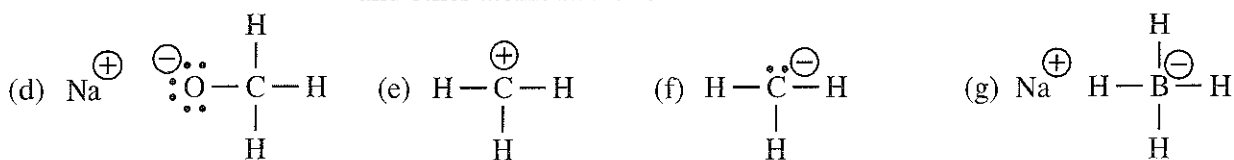
1-5 The symbols " δ^+ " and " δ^- " indicate bond polarity by showing partial charge. (In the arrow symbolism, the arrow should point to the partial negative charge.)



1-6 Non-zero formal charges are shown beside the atoms, circled for clarity.

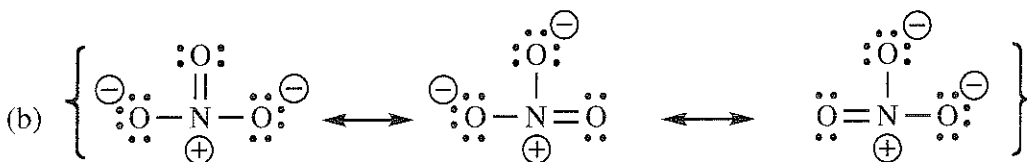
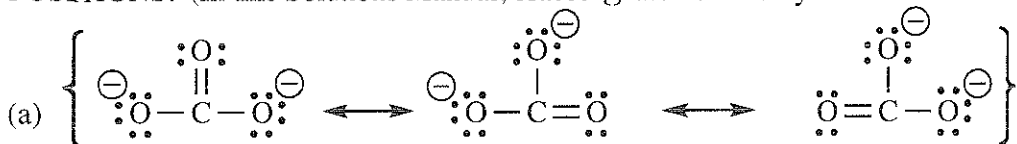


In (b) and (c), the chlorine is present as chloride ion. There is no covalent bond between chloride and other atoms in the formula.

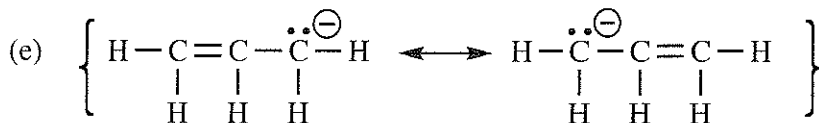
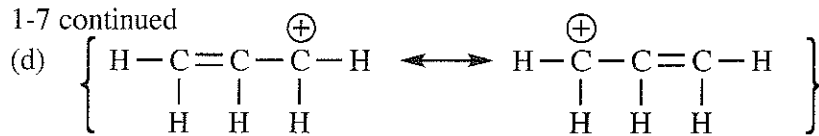


As shown in (d), (g), (h), and (k), alkali metals like sodium and potassium form only ionic bonds, never covalent bonds.

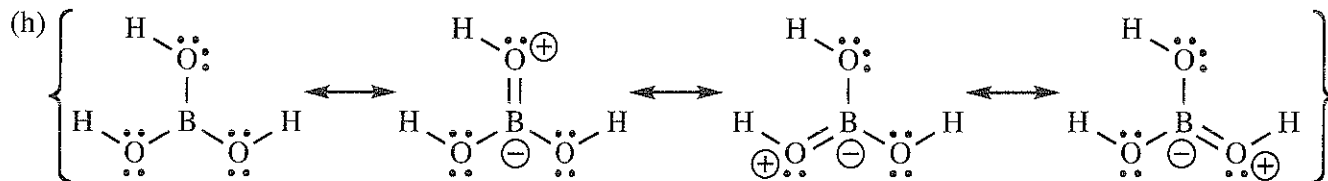
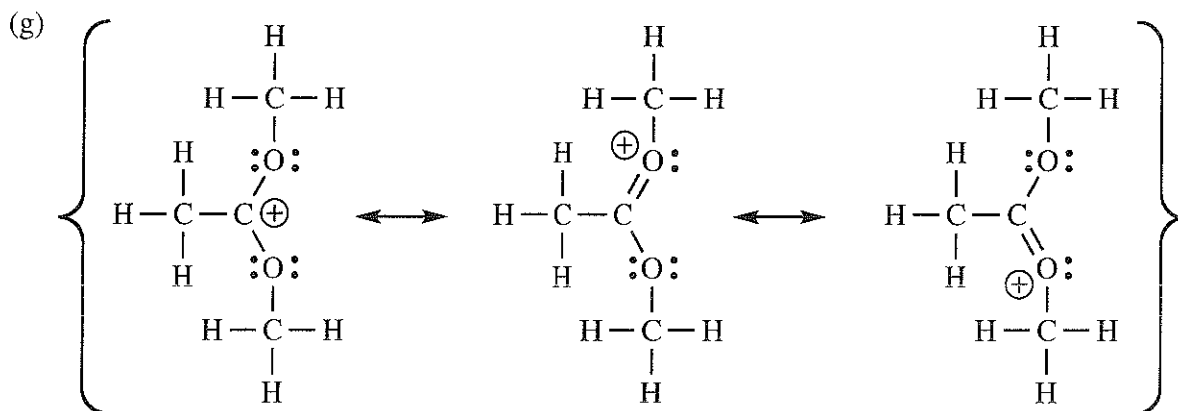
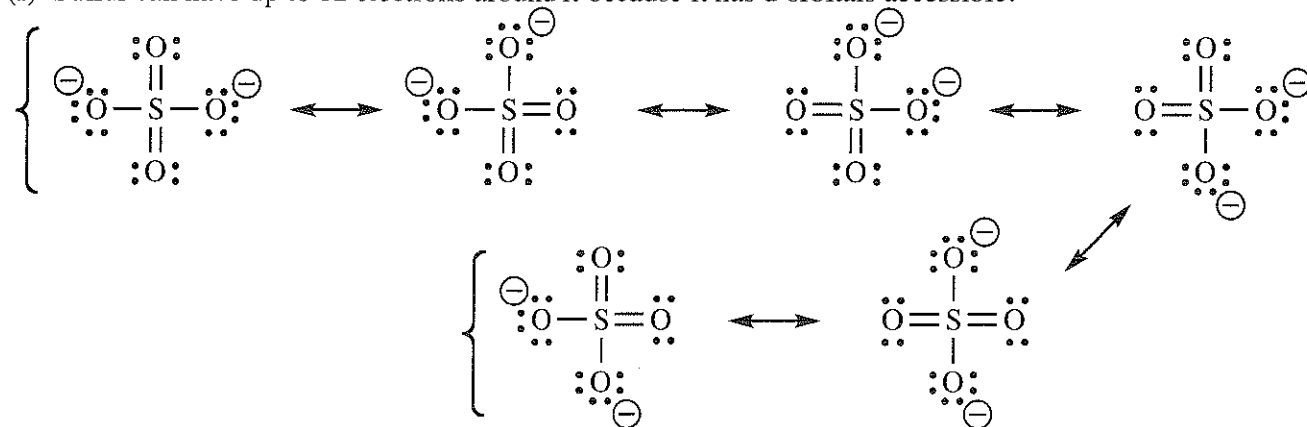
1-7 Resonance forms in which all atoms have full octets are the most significant contributors. In resonance forms, ALL ATOMS KEEP THEIR POSITIONS—ONLY ELECTRONS ARE SHOWN IN DIFFERENT POSITIONS. (In this Solutions Manual, braces $\{ \}$ are commonly used to denote resonance forms.)



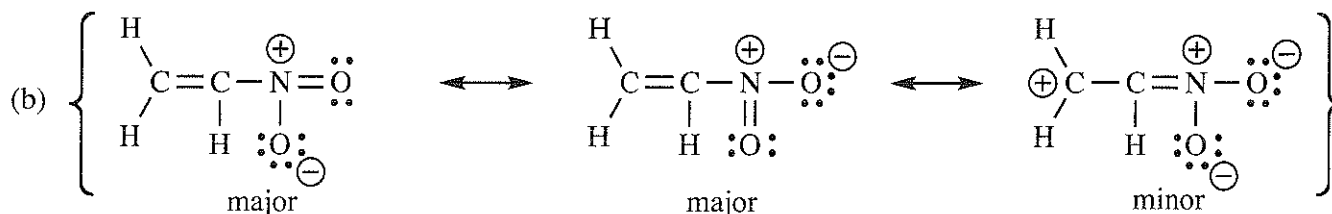
1-7 continued



(f) Sulfur can have up to 12 electrons around it because it has d orbitals accessible.

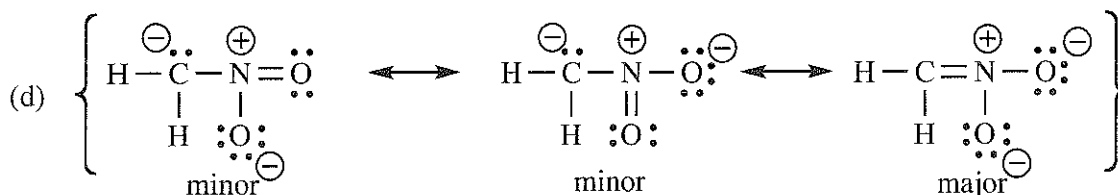
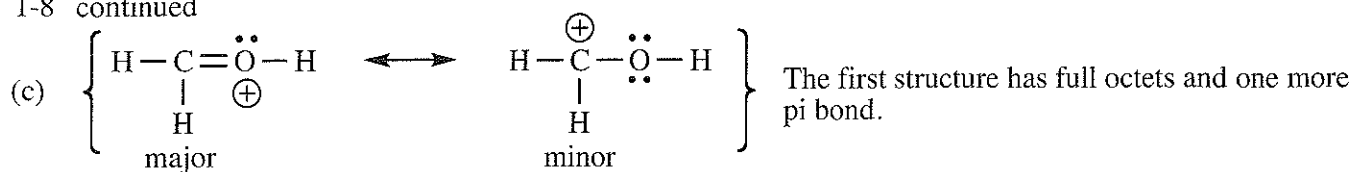


1-8 Major resonance contributors would have the lowest energy. The most important factors are: maximize full octets; maximize pi bonds; put negative charge on electronegative atoms; minimize charge separation—see the Problem-Solving Hint in text Section 1-9B. Part (a) has been solved in the text.

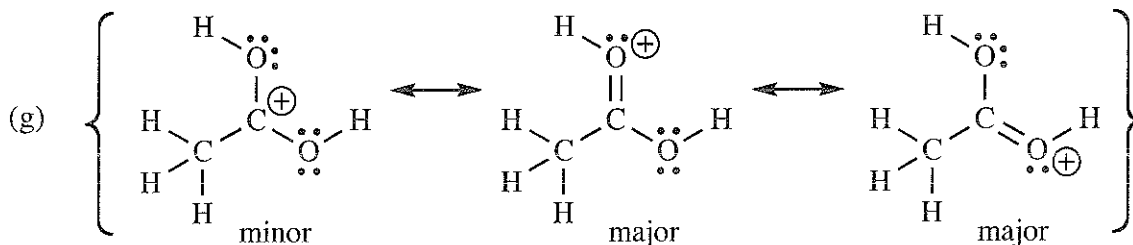
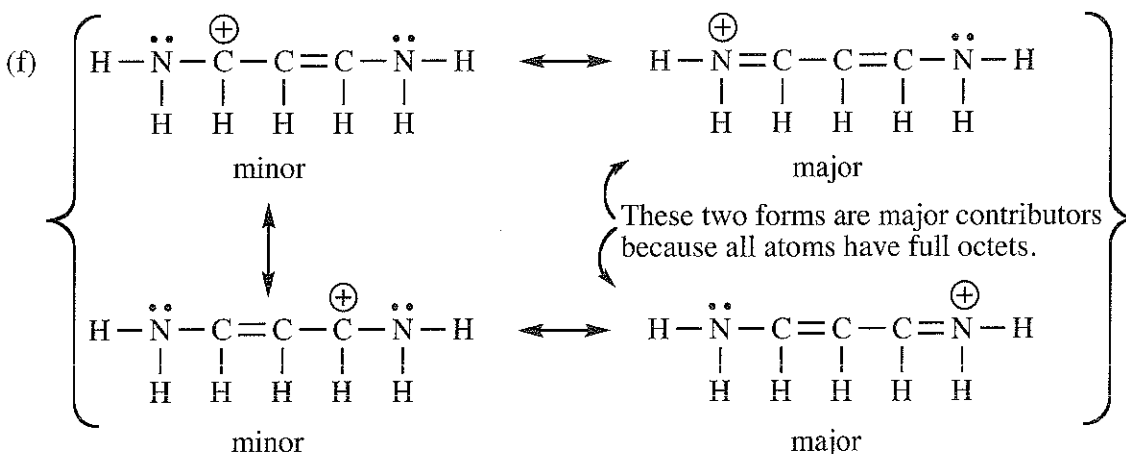
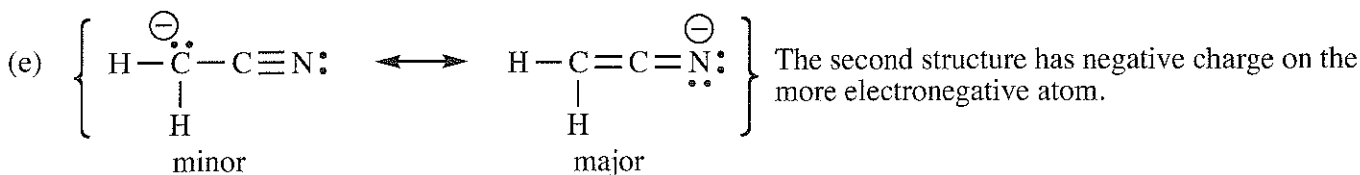


These first two forms have equivalent energy and are major because they have full octets, more bonds, and less charge separation than the minor contributor.

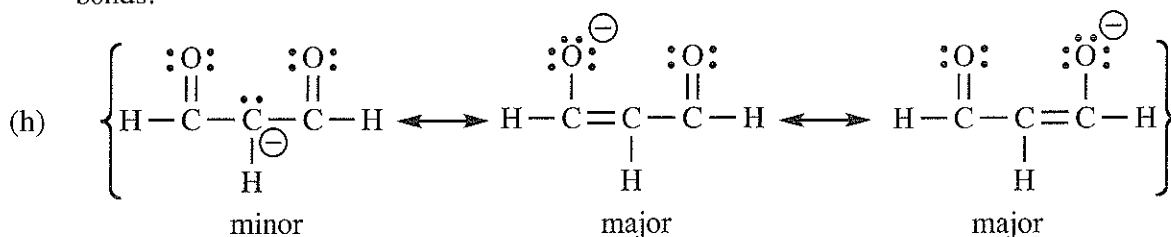
1-8 continued



All atoms have octets; same number of pi bonds; third structure has negative charge on the more electronegative oxygen atoms instead of carbon.

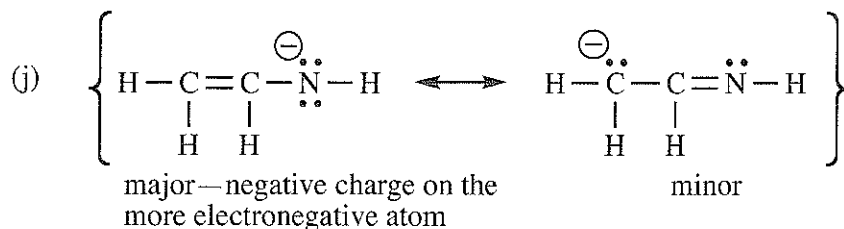
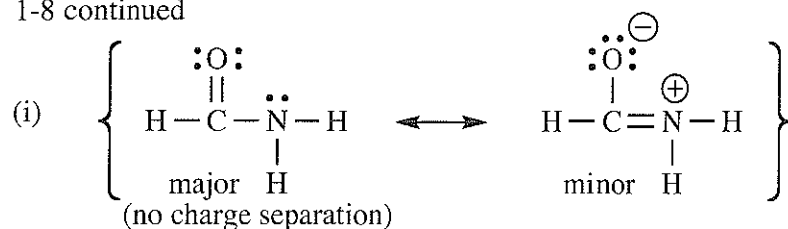


The latter two structures have equivalent energy and are major because they have full octets and more pi bonds.

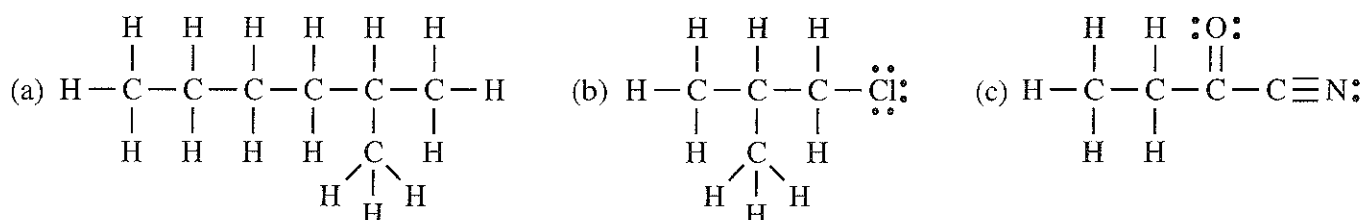


The latter two structures have equivalent energy and are major because the negative charge is on the more electronegative oxygen atom.

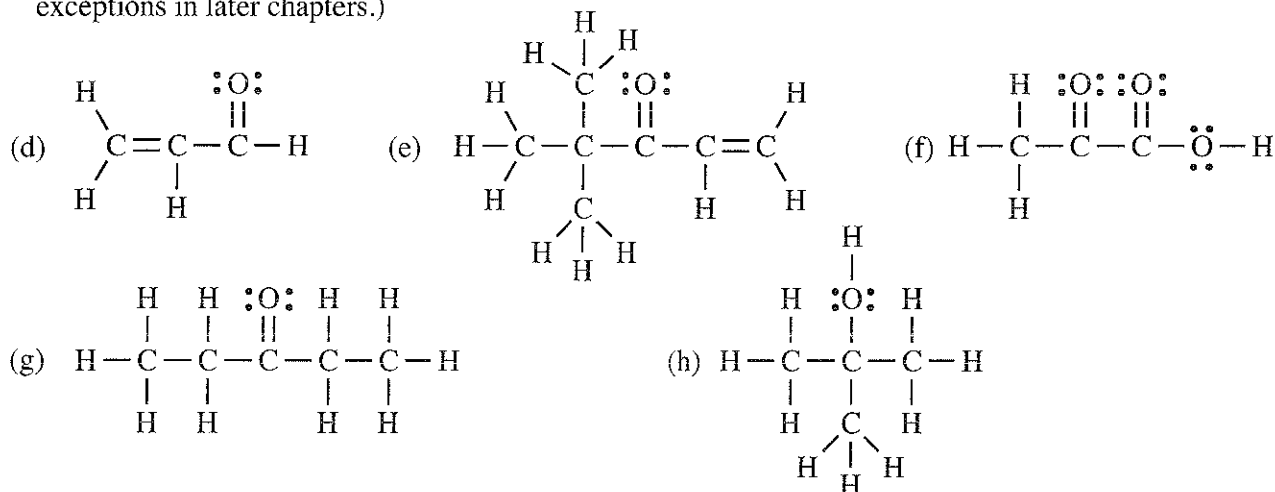
1-8 continued



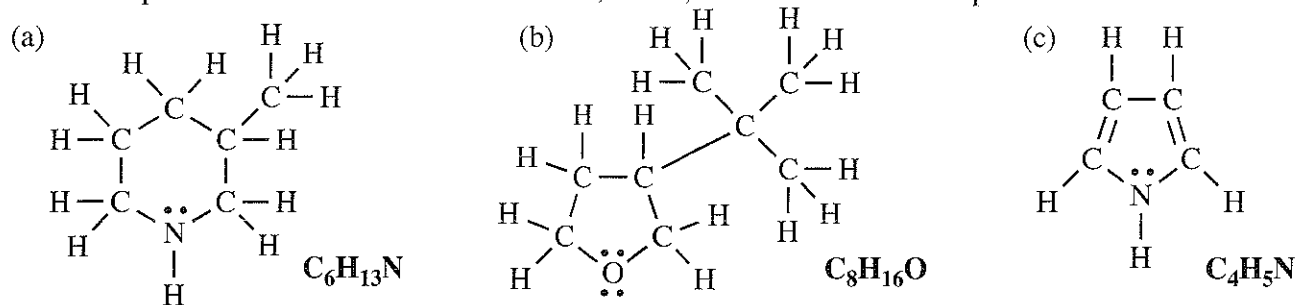
1-9 Your Lewis structures may *appear* different from these. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant. A Lewis structure is "complete" with unshared electron pairs shown.



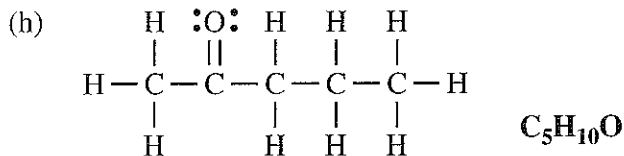
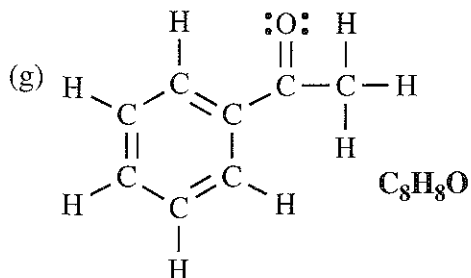
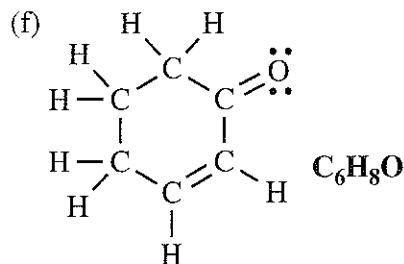
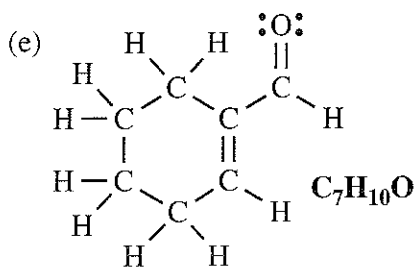
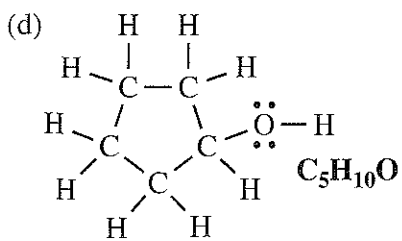
Always be alert for the implied double or triple bond. Remember that the normal valence of C is four bonds, nitrogen has three bonds, oxygen has two bonds, and hydrogen has one bond. The only exceptions to these valence rules are structures with formal charges. (We will see other unusual exceptions in later chapters.)



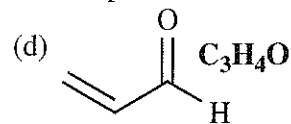
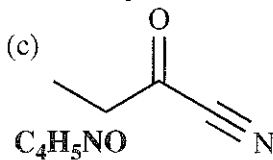
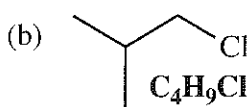
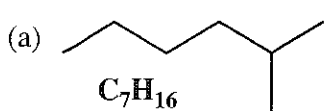
1-10 Complete Lewis structures show all atoms, bonds, and unshared electron pairs.



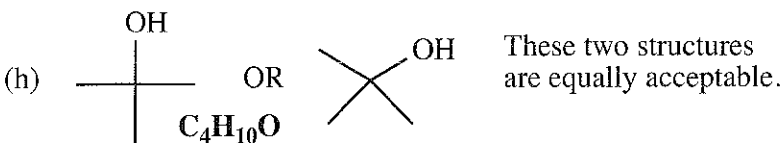
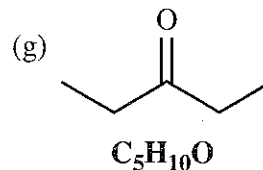
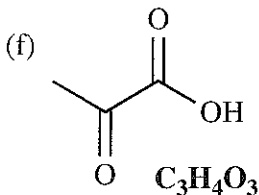
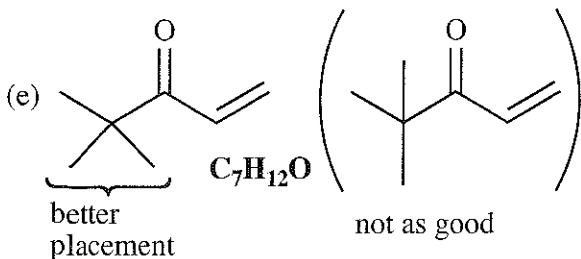
1-10 continued



1-11 Line-angle structures, sometimes called "stick" figures, usually omit unshared electron pairs.



H on C are usually not shown but this is an exception; it clarifies what ends this chain.



1-12 If the percent values do not sum to 100%, the remainder must be oxygen. Assume 100 g of sample; percents then translate directly to grams of each element.

There are usually MANY possible structures for a molecular formula. Yours may be different from the examples shown here and they could still be correct.

(a) $\frac{40.0 \text{ g C}}{12.0 \text{ g/mole}} = 3.33 \text{ moles C} \div 3.33 \text{ moles} = 1 \text{ C}$

$\frac{6.67 \text{ g H}}{1.01 \text{ g/mole}} = 6.60 \text{ moles H} \div 3.33 \text{ moles} = 1.98 \approx 2 \text{ H}$

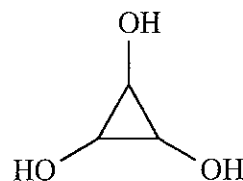
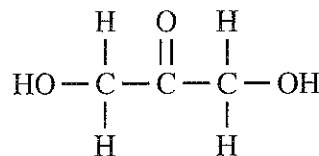
$\frac{53.33 \text{ g O}}{16.0 \text{ g/mole}} = 3.33 \text{ moles O} \div 3.33 \text{ moles} = 1 \text{ O}$

empirical formula = $\boxed{CH_2O}$ \Rightarrow empirical weight = 30.02

molecular weight = 90, three times the empirical weight \Rightarrow

three times the empirical formula = molecular formula = $\boxed{C_3H_6O_3}$

some possible structures:



Other structures are possible.

1-12 continued

$$(b) \frac{32.0 \text{ g C}}{12.0 \text{ g/mole}} = 2.67 \text{ moles C} \div 1.34 \text{ moles} = 1.99 \approx 2 \text{ C}$$

$$\frac{6.67 \text{ g H}}{1.01 \text{ g/mole}} = 6.60 \text{ moles H} \div 1.34 \text{ moles} = 4.93 \approx 5 \text{ H}$$

$$\frac{18.7 \text{ g N}}{14.0 \text{ g/mole}} = 1.34 \text{ moles N} \div 1.34 \text{ moles} = 1 \text{ N}$$

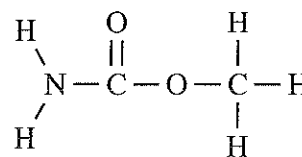
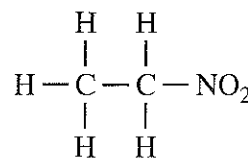
$$\frac{42.6 \text{ g O}}{16.0 \text{ g/mole}} = 2.66 \text{ moles O} \div 1.34 \text{ moles} = 1.99 \approx 2 \text{ O}$$

empirical formula = $\boxed{\text{C}_2\text{H}_5\text{NO}_2}$ \Rightarrow empirical weight = 75.05

molecular weight = 75, same as the empirical weight \Rightarrow

empirical formula = molecular formula = $\boxed{\text{C}_2\text{H}_5\text{NO}_2}$

some possible structures:



MANY other structures are possible.

$$(c) \frac{25.6 \text{ g C}}{12.0 \text{ g/mole}} = 2.13 \text{ moles C} \div 1.07 \text{ moles} = 1.99 \approx 2 \text{ C}$$

$$\frac{4.32 \text{ g H}}{1.01 \text{ g/mole}} = 4.28 \text{ moles H} \div 1.07 \text{ moles} = 4 \text{ H}$$

$$\frac{37.9 \text{ g Cl}}{35.45 \text{ g/mole}} = 1.07 \text{ moles Cl} \div 1.07 \text{ moles} = 1 \text{ Cl}$$

$$\frac{15.0 \text{ g N}}{14.0 \text{ g/mole}} = 1.07 \text{ moles N} \div 1.07 \text{ moles} = 1 \text{ N}$$

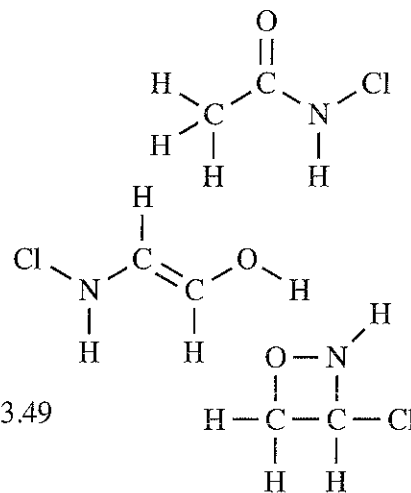
$$\frac{17.2 \text{ g O}}{16.0 \text{ g/mole}} = 1.07 \text{ moles O} \div 1.07 \text{ moles} = 1 \text{ O}$$

empirical formula = $\boxed{\text{C}_2\text{H}_4\text{ClNO}}$ \Rightarrow empirical weight = 93.49

molecular weight = 93, same as the empirical weight \Rightarrow

empirical formula = molecular formula = $\boxed{\text{C}_2\text{H}_4\text{ClNO}}$

some possible structures:



MANY other structures are possible.

$$(d) \frac{38.4 \text{ g C}}{12.0 \text{ g/mole}} = 3.20 \text{ moles C} \div 1.60 \text{ moles} = 2 \text{ C}$$

$$\frac{4.80 \text{ g H}}{1.01 \text{ g/mole}} = 4.75 \text{ moles H} \div 1.60 \text{ moles} = 2.97 \approx 3 \text{ H}$$

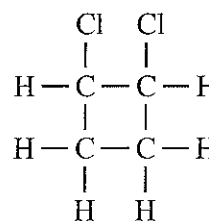
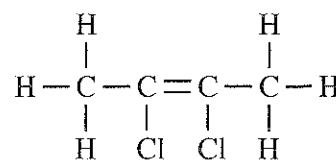
$$\frac{56.8 \text{ g Cl}}{35.45 \text{ g/mole}} = 1.60 \text{ moles Cl} \div 1.60 \text{ moles} = 1 \text{ Cl}$$

empirical formula = $\boxed{\text{C}_2\text{H}_3\text{Cl}}$ \Rightarrow empirical weight = 62.45

molecular weight = 125, twice the empirical weight \Rightarrow

twice the empirical formula = molecular formula = $\boxed{\text{C}_4\text{H}_6\text{Cl}_2}$

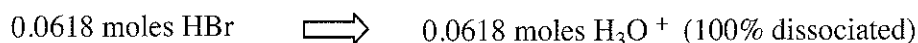
some possible structures:



MANY other structures are possible.

1-13

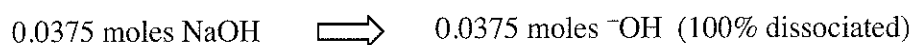
$$(a) \quad 5.00 \text{ g HBr} \times \frac{1 \text{ mole HBr}}{80.9 \text{ g HBr}} = 0.0618 \text{ moles HBr}$$



$$\frac{0.0618 \text{ moles H}_3\text{O}^+}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{0.618 \text{ moles H}_3\text{O}^+}{1 \text{ L solution}}$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} (0.618) = \boxed{0.209}$$

$$(b) \quad 1.50 \text{ g NaOH} \times \frac{1 \text{ mole NaOH}}{40.0 \text{ g NaOH}} = 0.0375 \text{ moles NaOH}$$



$$\frac{0.0375 \text{ moles } ^-\text{OH}}{50. \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{0.75 \text{ moles } ^-\text{OH}}{1 \text{ L solution}} = 0.75 \text{ M}$$

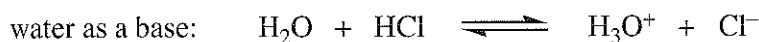
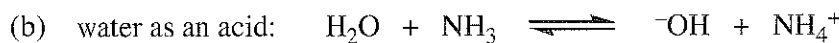
$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.75} = 1.33 \times 10^{-14}$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} (1.33 \times 10^{-14}) = \boxed{13.88}$$

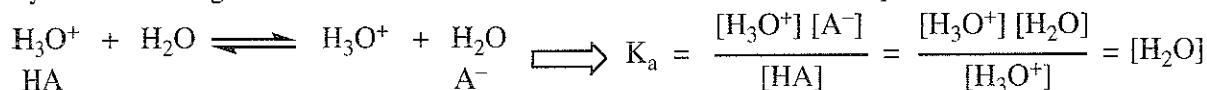
(The number of decimal places in a pH value is the number of significant figures.)

1-14

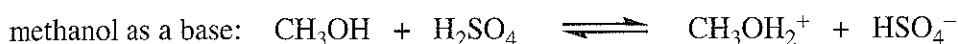
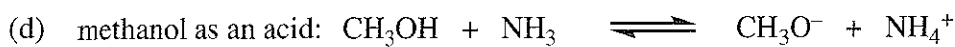
(a) By definition, an acid is any species that can donate a proton. Ammonia has a proton bonded to nitrogen, so ammonia can be an acid (although a very weak one). A base is a proton acceptor, that is, it must have a pair of electrons to share with a proton; in theory, any atom with an unshared electron pair can be a base. The nitrogen in ammonia has an unshared electron pair so ammonia is basic. In water, ammonia is too weak an acid to give up its proton; instead, it acts as a base and pulls a proton from water to a small extent.



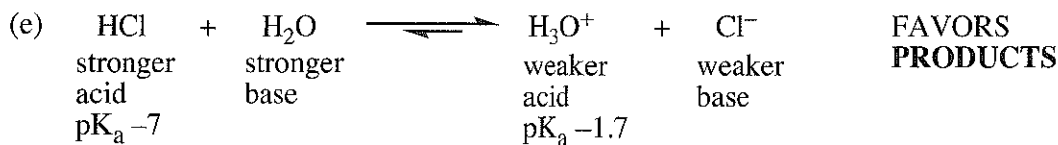
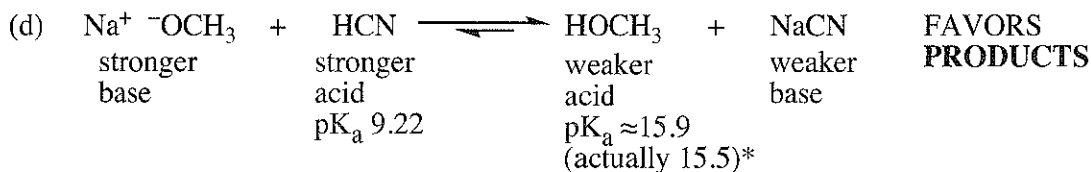
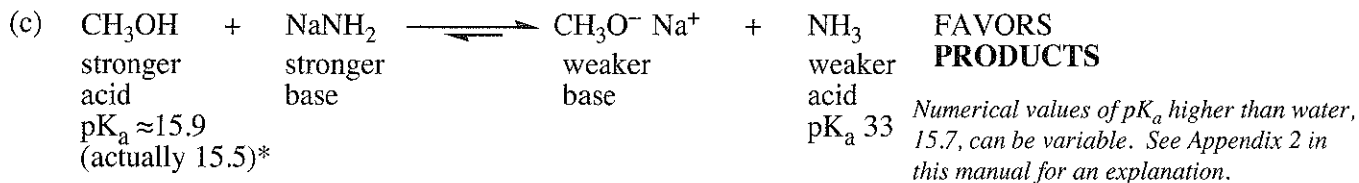
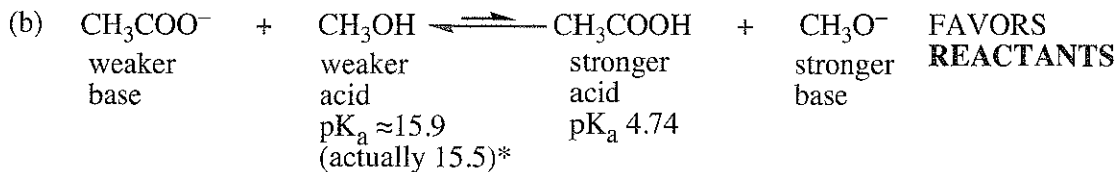
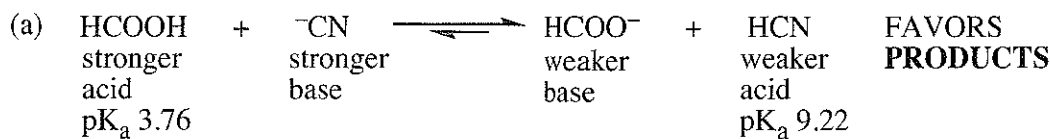
(c) Hydronium acting as an acid in water solution will have this chemical equation:



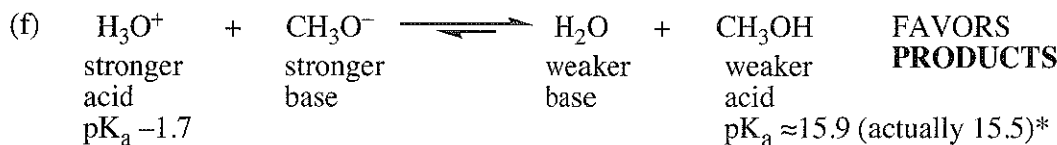
$$[\text{H}_2\text{O}] = \frac{1000 \text{ g H}_2\text{O}}{1 \text{ L H}_2\text{O}} \times \frac{1 \text{ mole H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = \underline{55.55 \text{ M}} = K_a \quad \Longrightarrow \quad \text{p}K_a = -\log(55.55) = \underline{-1.74}$$



1-15

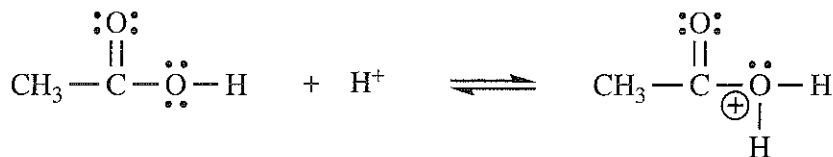


The first reaction in text Table 1-5 shows the K_{eq} for this reaction is 1×10^7 , favoring products.



*The ninth reaction in Table 1-5 shows the pK_a of a structure similar to CH_3OH is 15.9, so it is reasonable to infer that the pK_a value of CH_3OH is approximately the same. (Text Appendix 4 gives a value of 15.5.) Using either value indicates that CH_3OH is the weaker acid, so products are favored.

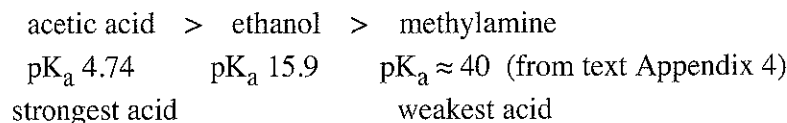
1-16



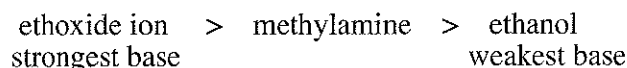
Protonation of the double-bonded oxygen gives three resonance forms (as shown in Solved Problem 1-5(c)); protonation of the single-bonded oxygen does not give any significant resonance forms, just the structure shown; it is not stabilized by resonance. In general, the more resonance forms a species has, the more stable it is, so the proton would bond to the oxygen that gives a more stable species, that is, the double-bonded oxygen.

1-17 In Solved Problem 1-4, the structure of methylamine is shown to be similar to ammonia. It is reasonable to infer that their acid-base properties are also similar.

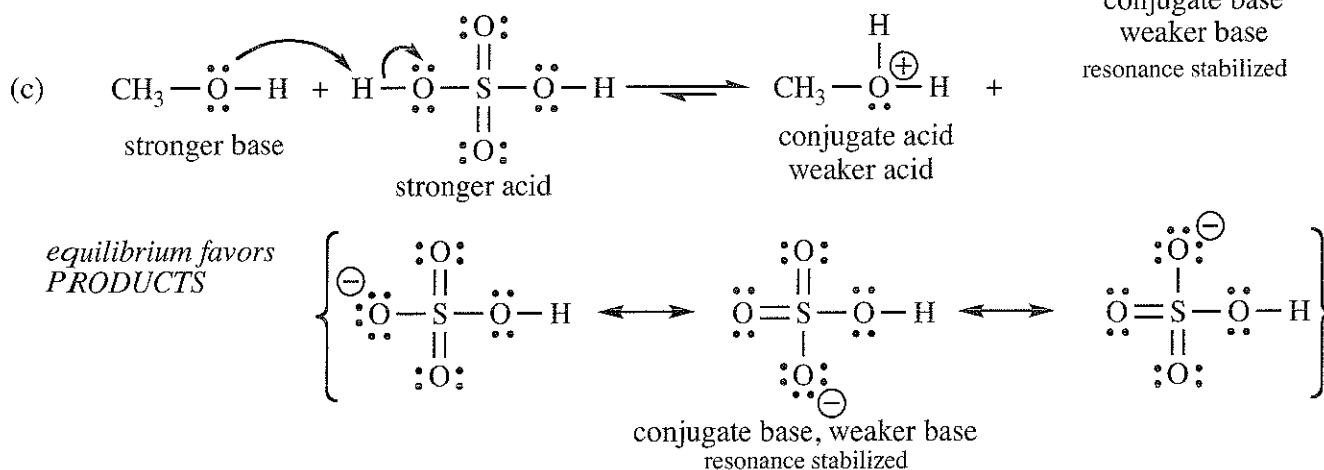
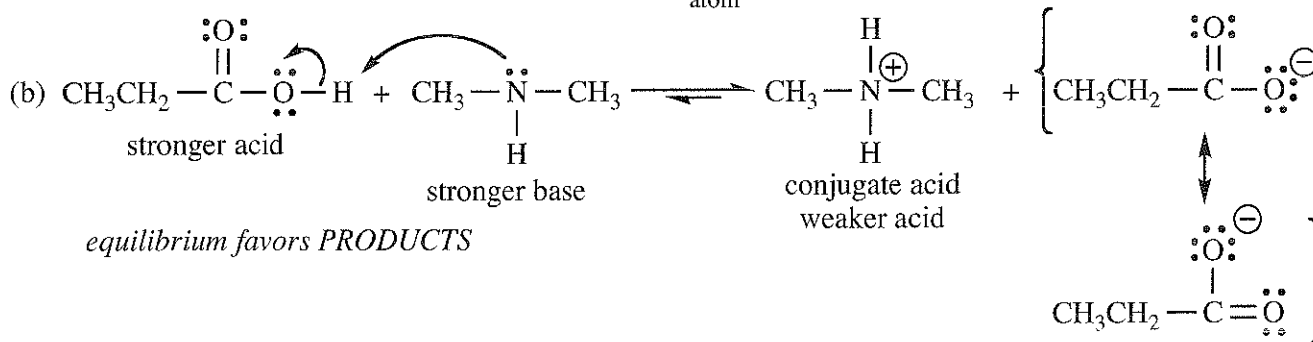
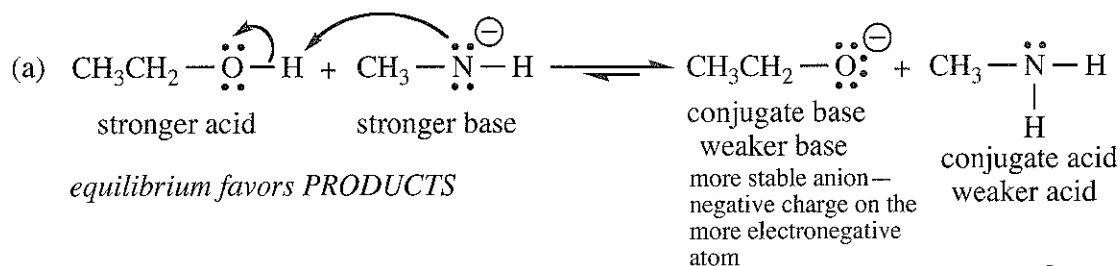
(a) This problem can be viewed in two ways. 1) Quantitatively, the pK_a values determine the order of acidity. 2) Qualitatively, the stabilities of the conjugate bases determine the order of acidity (see Solved Problem 1-4 for structures): the conjugate base of acetic acid, acetate ion, is resonance-stabilized, so acetic acid is the most acidic; the conjugate base of ethanol has a negative charge on a very electronegative oxygen atom; the conjugate base of methylamine has a negative charge on a mildly electronegative nitrogen atom and is therefore the least stabilized, so methylamine is the least acidic. (The first two pK_a values are from text Table 1-5.)



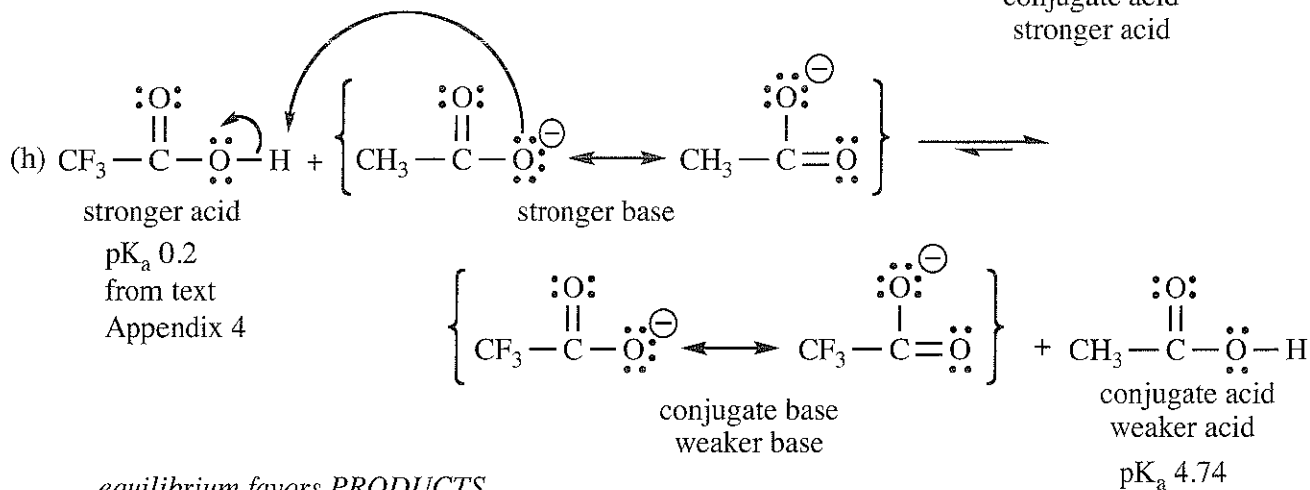
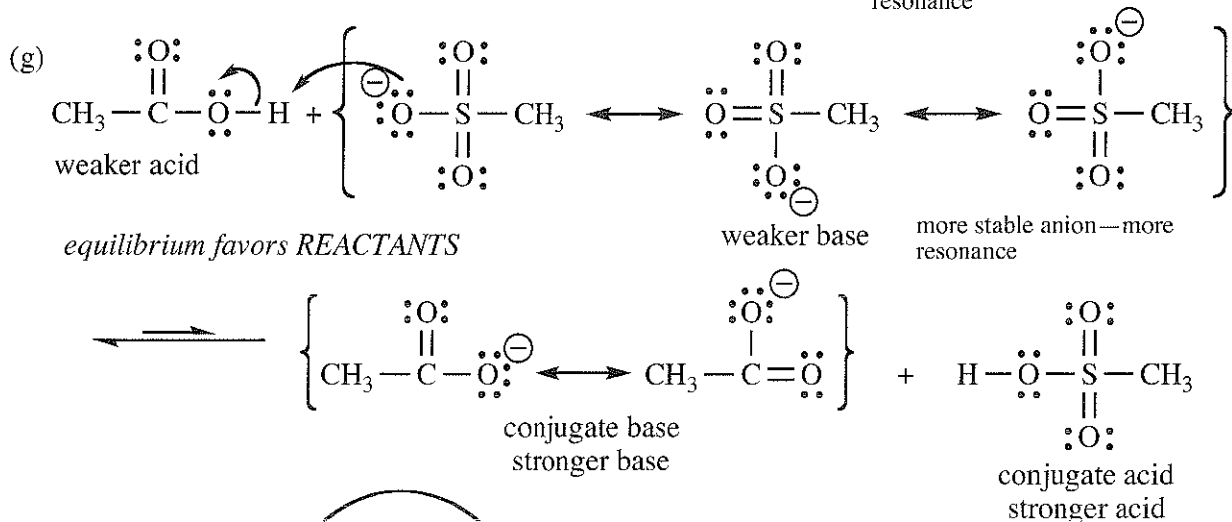
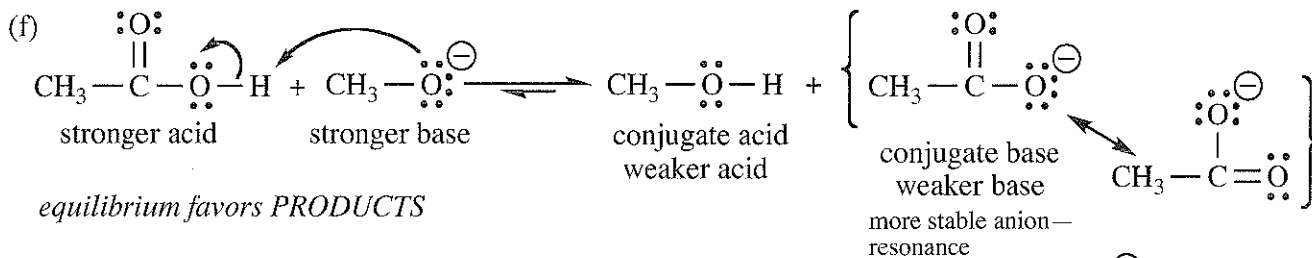
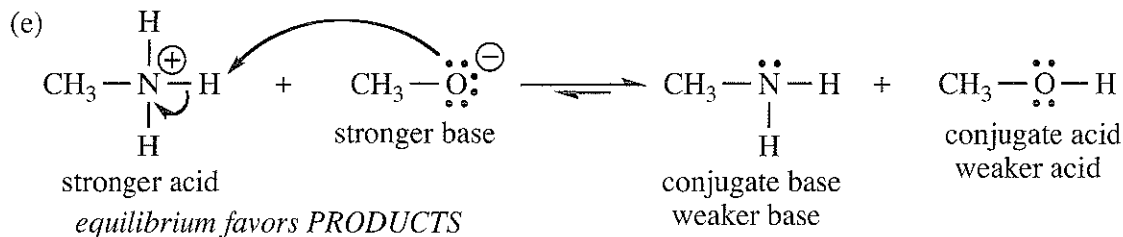
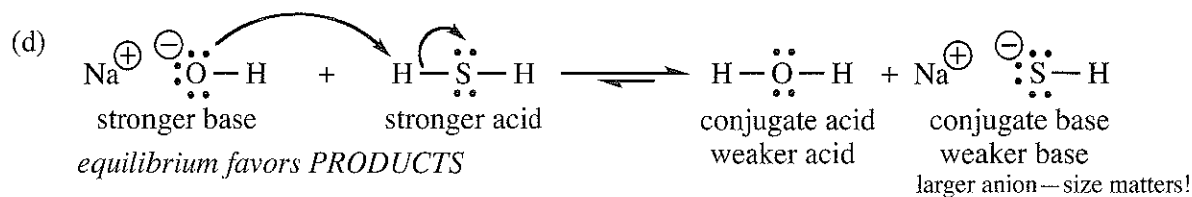
(b) Ethoxide ion is the conjugate base of ethanol, so it must be a stronger base than ethanol; Solved Problem 1-4 and text Table 1-5 indicate ethoxide is analogous to hydroxide in base strength. Methylamine has pK_b 3.36. The basicity of methylamine is between the basicity of ethoxide ion and ethanol.



1-18 Curved arrows show electron movement, as described in text Section 1-14.

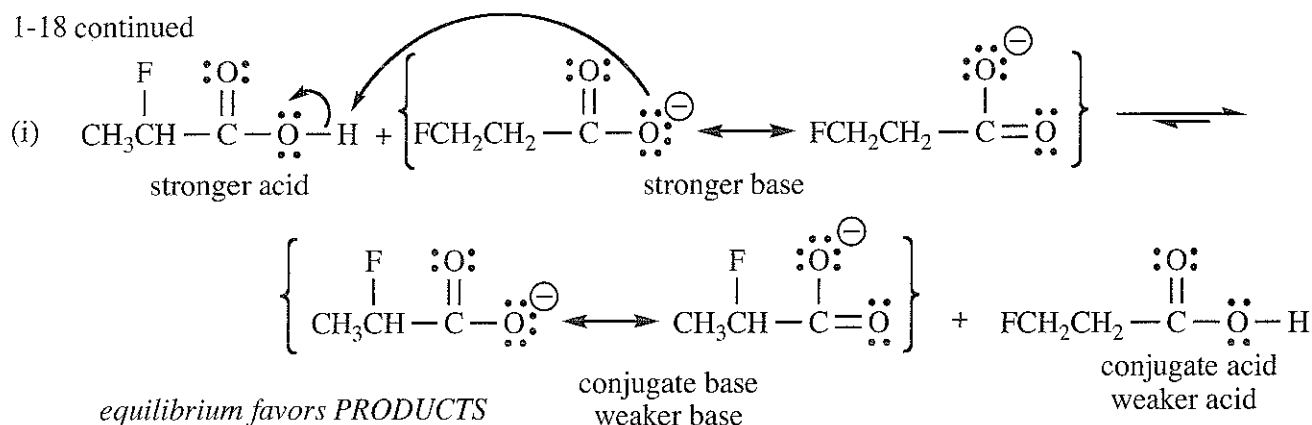


1-18 continued

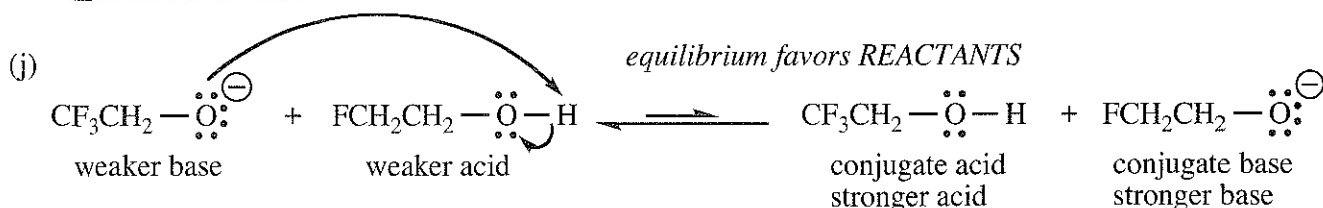


The presence of electronegative atoms like F will make an acid stronger by the inductive effect.

1-18 continued

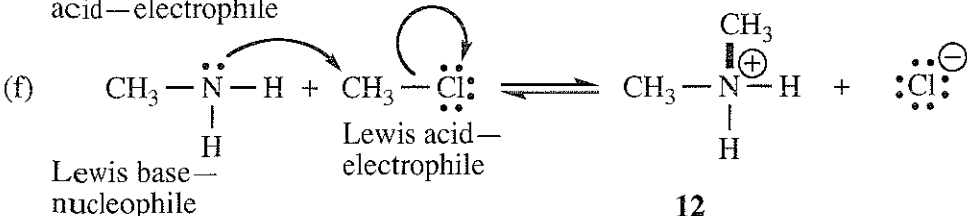
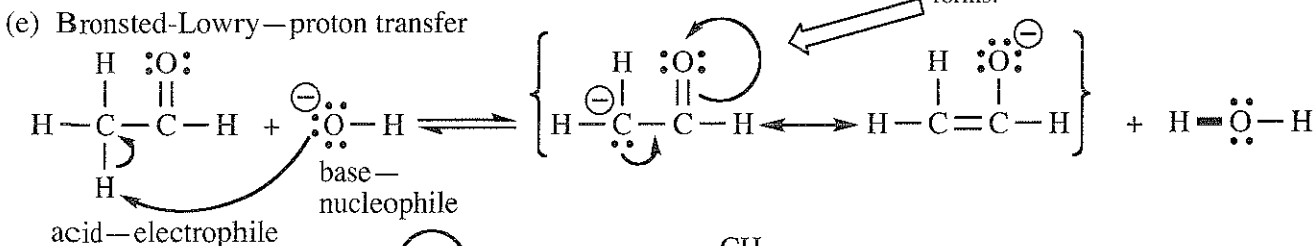
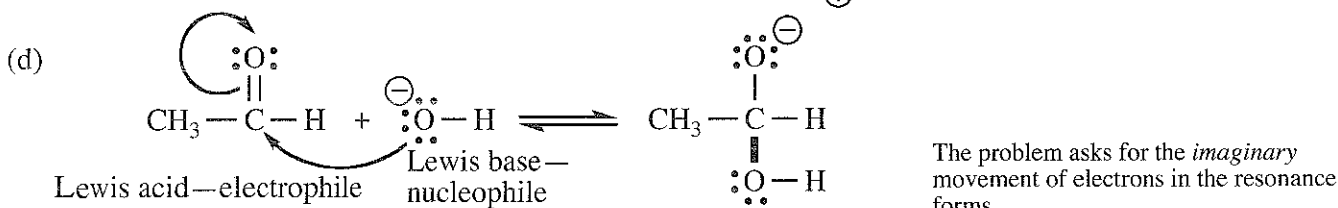
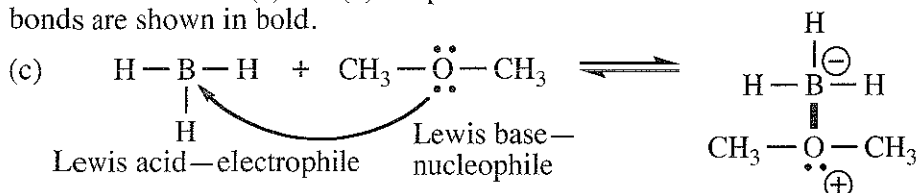


The presence of electronegative atoms like F will make an acid stronger by the inductive effect. The closer the electronegative atom is to the acidic group, the stronger its effect. The acid with the F on the second carbon is a stronger acid than the one with the F on the third carbon. From the point of view of the anions, the anion with the F closer to it is more stable, that is, a weaker base, leading to the same conclusion about which side is favored.

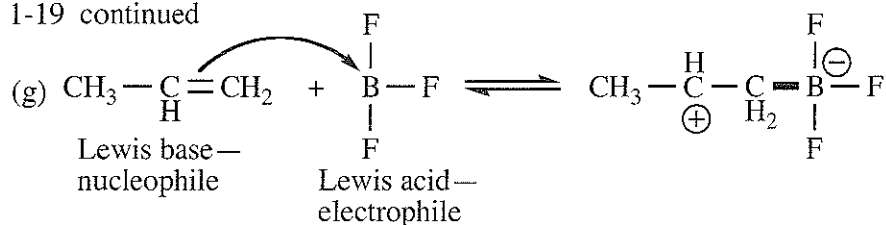


The presence of electronegative atoms like F will make an acid stronger by the inductive effect. Three F atoms will make a stronger acid than just one F atom. From the point of view of the anions, the anion with three F atoms is more stable, that is, a weaker base. None of these structures has other resonance forms.

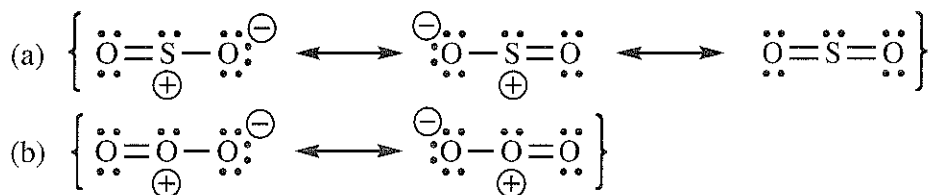
1-19 Solutions for (a) and (b) are presented in the Solved Problem in the text. Here, the newly formed bonds are shown in bold.



1-19 continued



1-20



(c) The last resonance form of SO_2 has no equivalent form in O_3 . Sulfur, a third row element, can have more than eight electrons around it because of d orbitals, whereas oxygen, a second row element, must adhere strictly to the octet rule.

1-21 (a) CARBON! (the best element) (b) oxygen (c) phosphorus (d) chlorine

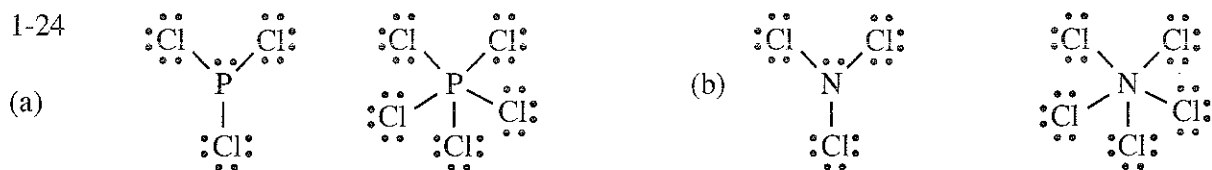
1-22

valence $e^- \rightarrow$	1	2	3	4	5	6	7	8
	H							He ($2e^-$)
	Li	Be	B	C	N	O	F	Ne
					P	S	Cl	
							Br	
							I	

1-23

- (a) ionic only (b) covalent ($\text{H}-\text{O}^-$) and ionic ($\text{Na}^+ \text{ } ^-\text{OH}$)
 (c) covalent ($\text{H}-\text{C}$ and $\text{C}-\text{Li}$), but the $\text{C}-\text{Li}$ bond is strongly polarized
 (d) covalent only (e) covalent ($\text{H}-\text{C}$ and $\text{C}-\text{O}^-$) and ionic ($\text{Na}^+ \text{ } ^-\text{OCH}_3$)
 (f) covalent ($\text{H}-\text{C}$ and $\text{C}=\text{O}$ and $\text{C}-\text{O}^-$) and ionic ($\text{HCO}_2^- \text{ } \text{Na}^+$) (g) covalent only

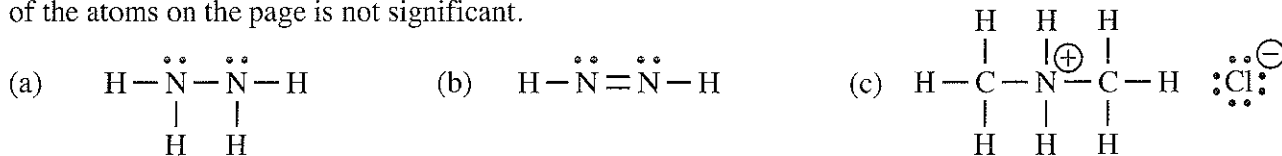
1-24



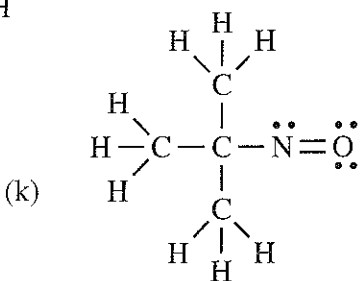
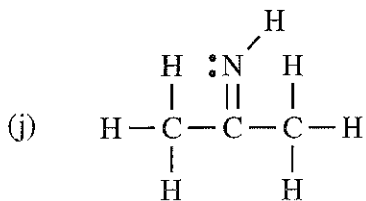
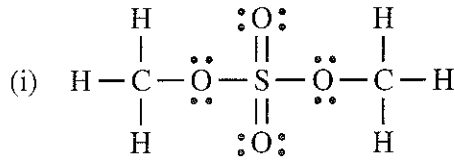
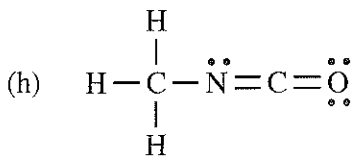
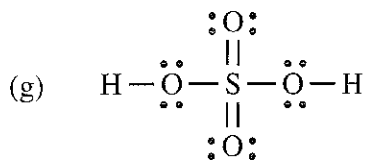
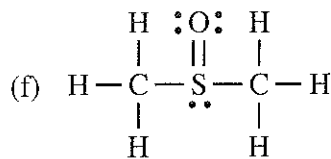
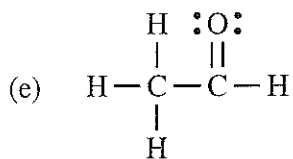
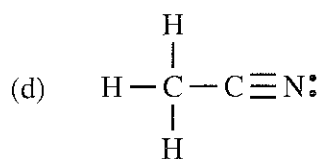
CANNOT EXIST

NCl_5 violates the octet rule; nitrogen can have no more than eight electrons (or four atoms) around it. Phosphorus, a third-row element, can have more than eight electrons because phosphorus can use d orbitals in bonding, so PCl_5 is a stable, isolable compound.

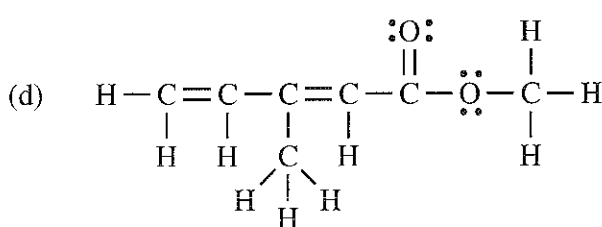
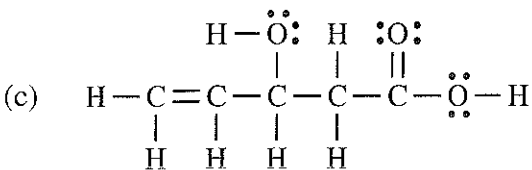
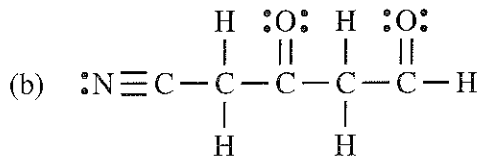
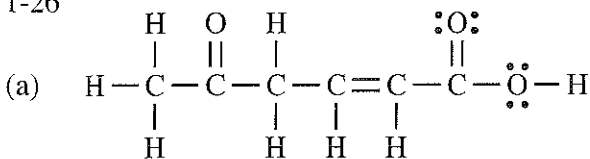
1-25 Your Lewis structures may look different from these. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant.



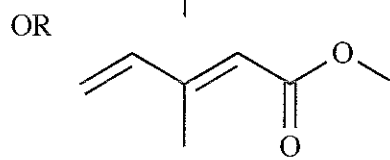
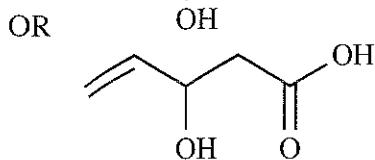
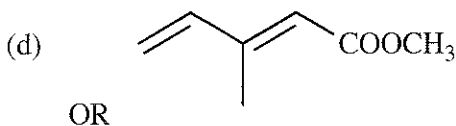
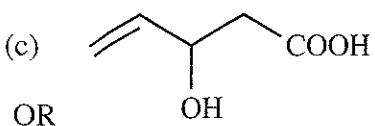
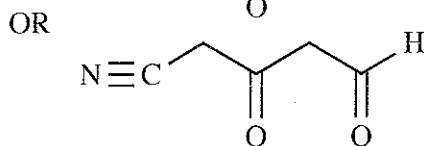
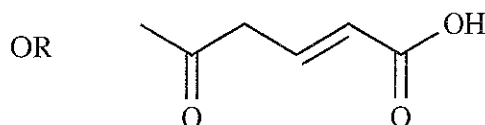
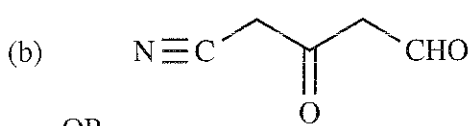
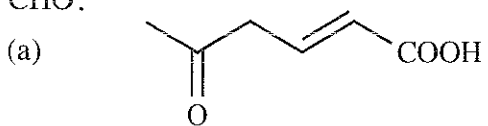
1-25 continued



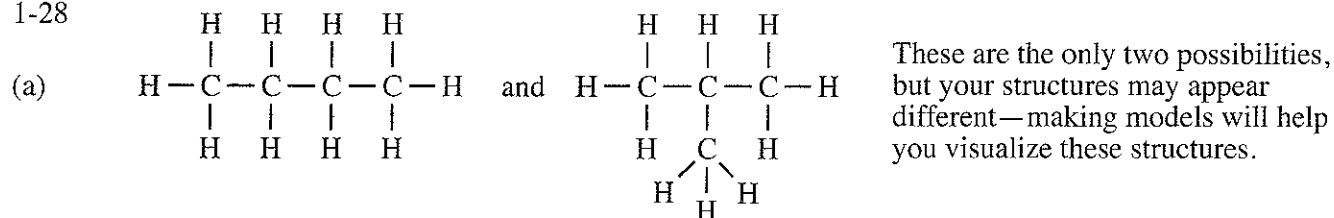
1-26



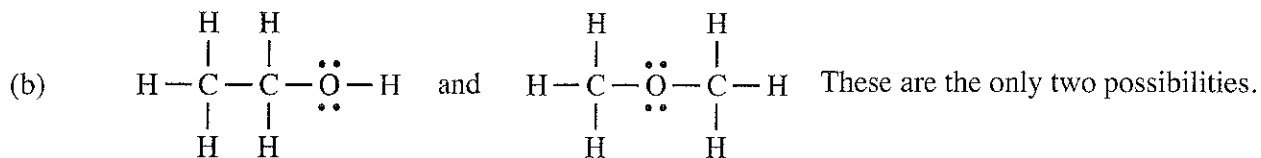
1-27 In each set below, the second structure is a more correct line formula. Since chemists are human (surprise!), they will take shortcuts where possible; the first structure in each pair uses a common abbreviation, either COOH or CHO. Make sure you understand that COOH does not stand for C—O—O—H. Likewise for CHO.



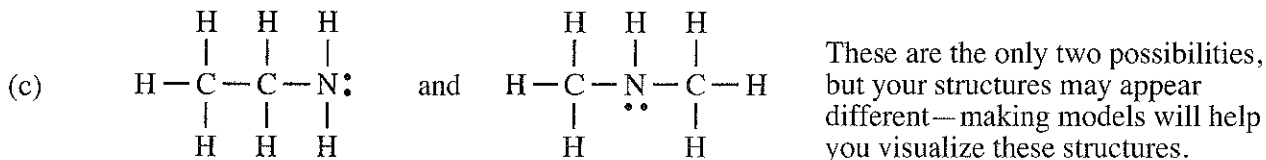
1-28



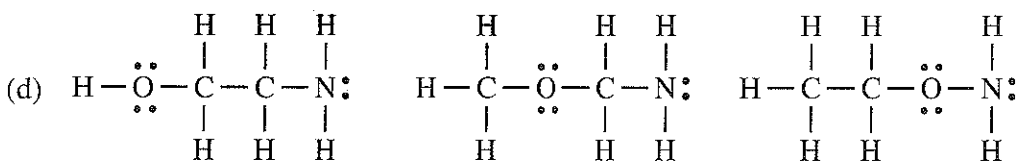
These are the only two possibilities, but your structures may appear different—making models will help you visualize these structures.



These are the only two possibilities.

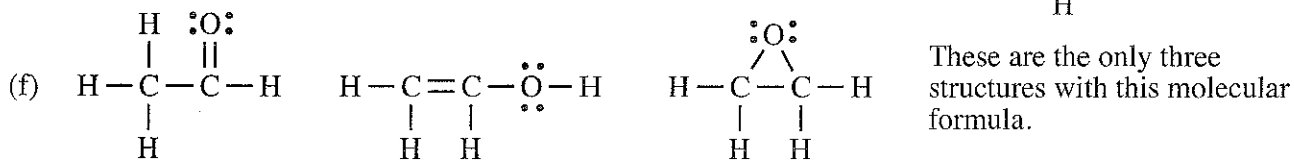
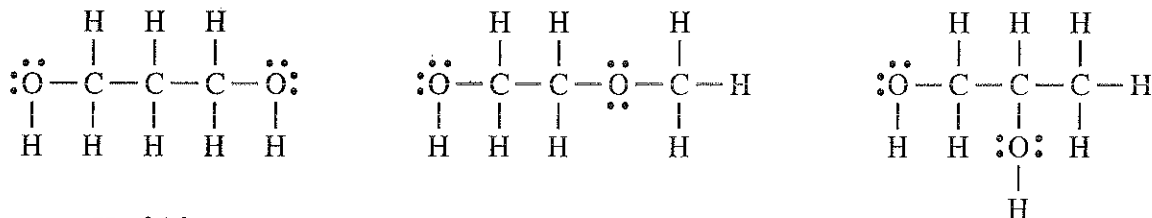


These are the only two possibilities, but your structures may appear different—making models will help you visualize these structures.



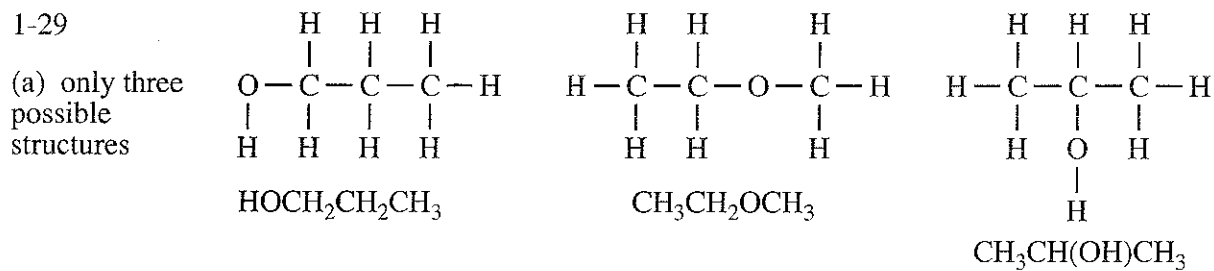
Think of all the ways an oxygen could be added to the structures in (c). There are many more!

(e) There are several other possibilities as well. Your answer may be correct even if it does not appear here. Check with others in your study group.



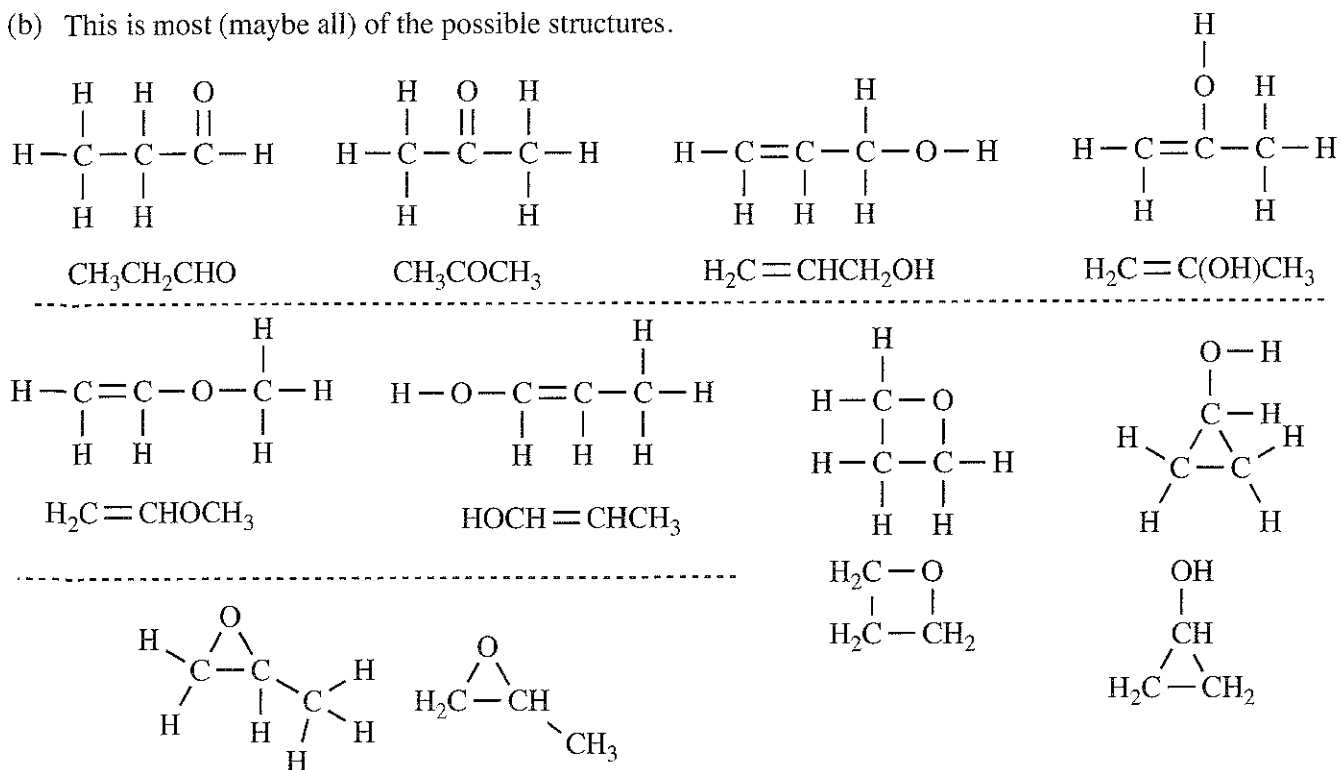
These are the only three structures with this molecular formula.

1-29



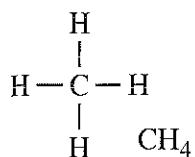
1-29 continued

(b) This is most (maybe all) of the possible structures.

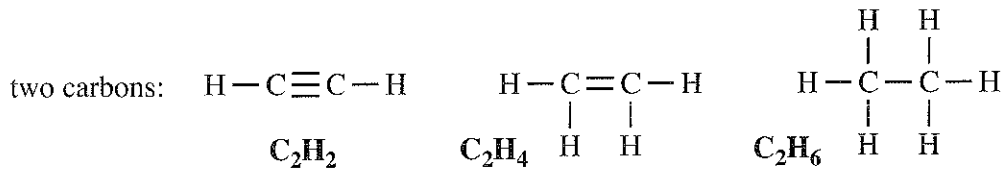


1-30 General rule: *molecular formulas of stable hydrocarbons must have an even number of hydrogens.*
The formula CH_2 does not have enough atoms to bond with the four orbitals of carbon.

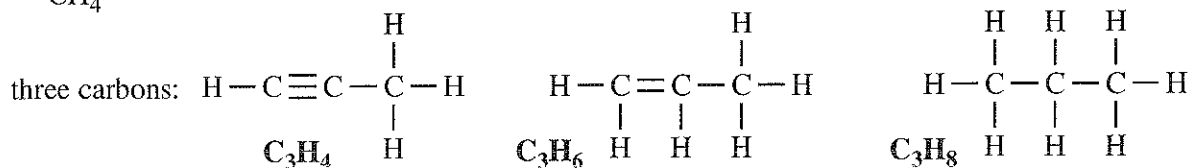
one carbon:



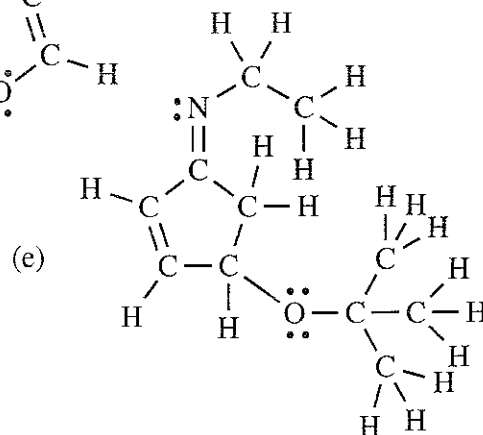
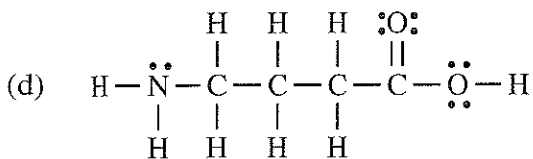
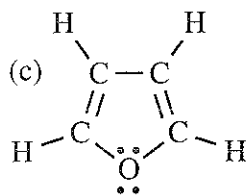
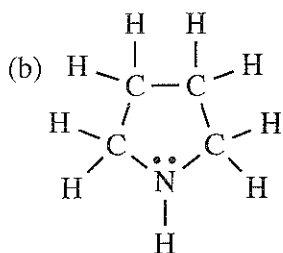
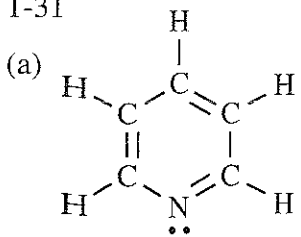
two carbons:

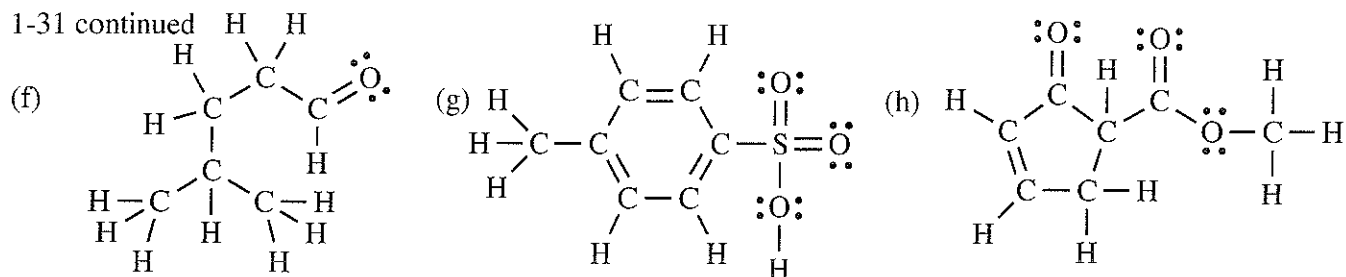


three carbons:



1-31





1-32 (a) C_5H_5N (b) C_4H_9N (c) C_4H_4O (d) $C_4H_9NO_2$ (e) $C_{11}H_{19}NO$

(f) $C_6H_{12}O$ (g) $C_7H_8O_3S$ (h) $C_7H_8O_3$

1-33

(a) $100\% - 62.0\% C - 10.4\% H = 27.6\%$ oxygen

$$\frac{62.0 \text{ g C}}{12.0 \text{ g/mole}} = 5.17 \text{ moles C} \div 1.73 \text{ moles} = 2.99 \approx 3 \text{ C}$$

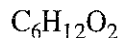
$$\frac{10.4 \text{ g H}}{1.01 \text{ g/mole}} = 10.3 \text{ moles H} \div 1.73 \text{ moles} = 5.95 \approx 6 \text{ H}$$

$$\frac{27.6 \text{ g O}}{16.0 \text{ g/mole}} = 1.73 \text{ moles O} \div 1.73 \text{ moles} = 1 \text{ O}$$

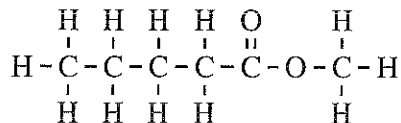
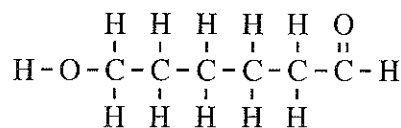
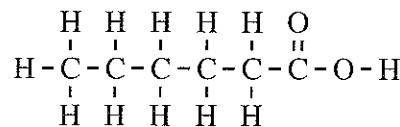
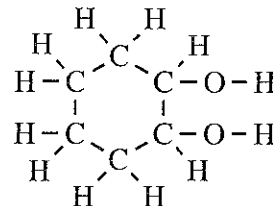
(b) empirical formula = C_3H_6O \Rightarrow empirical weight = 58

molecular weight = 117, about double the empirical weight

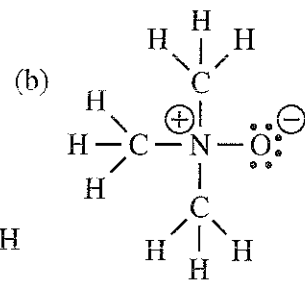
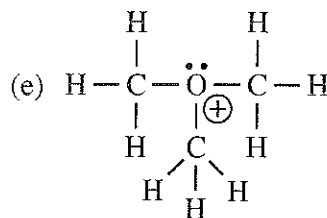
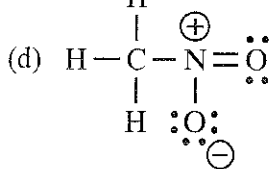
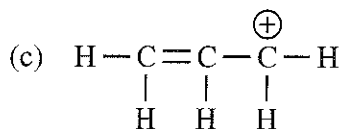
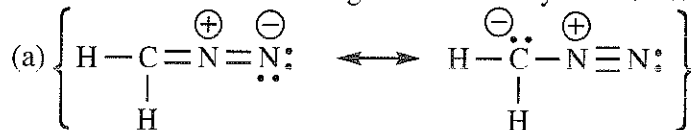
\Rightarrow double the empirical formula = molecular formula =



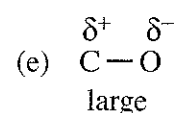
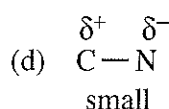
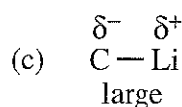
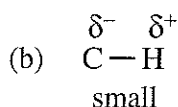
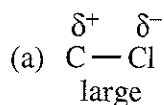
(c) some possible structures—MANY other structures are possible:



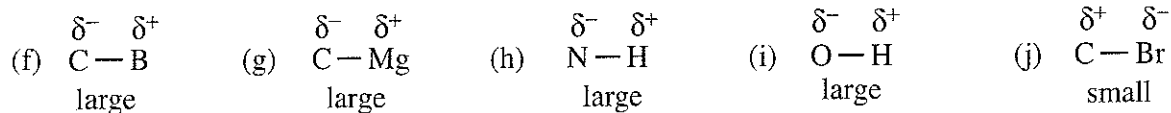
1-34 Non-zero formal charges are shown by the atoms.



1-35 The symbols " δ^+ " and " δ^- " indicate bond polarity by showing partial charge. Electronegativity differences greater than or equal to 0.5 are considered large.



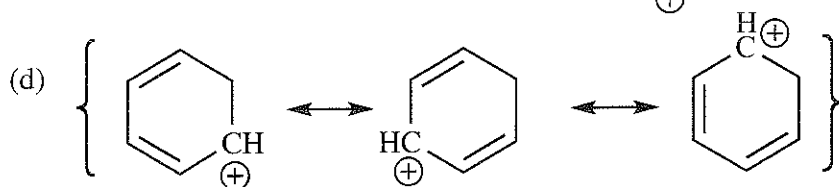
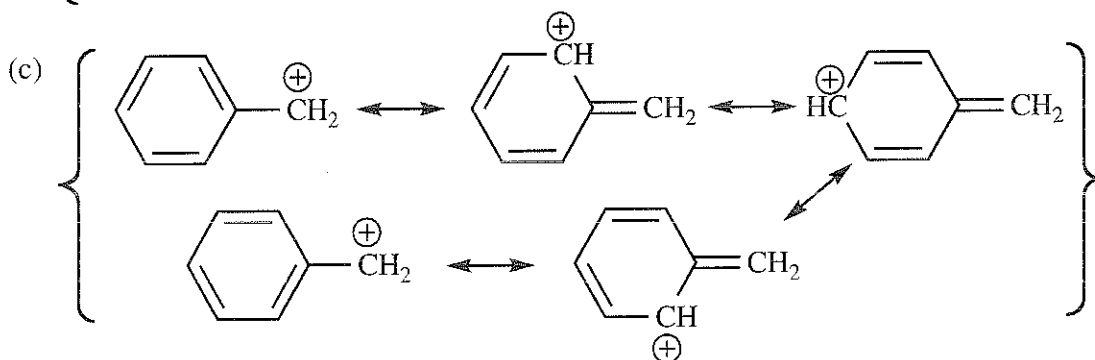
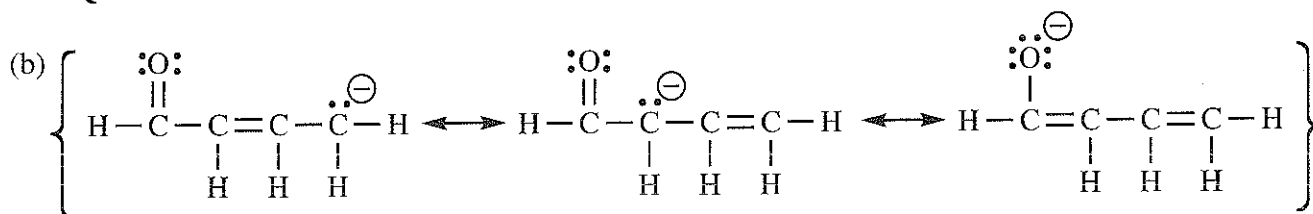
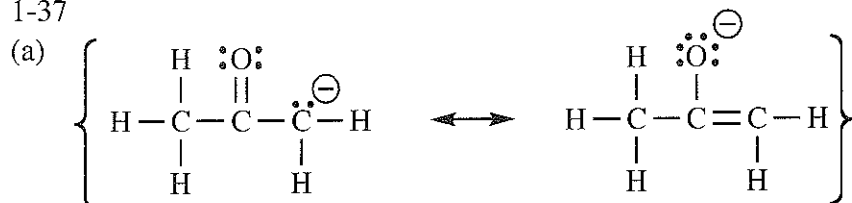
1-35 continued



1-36 Resonance forms must have atoms in identical positions. If any atom moves position, it is a different structure.

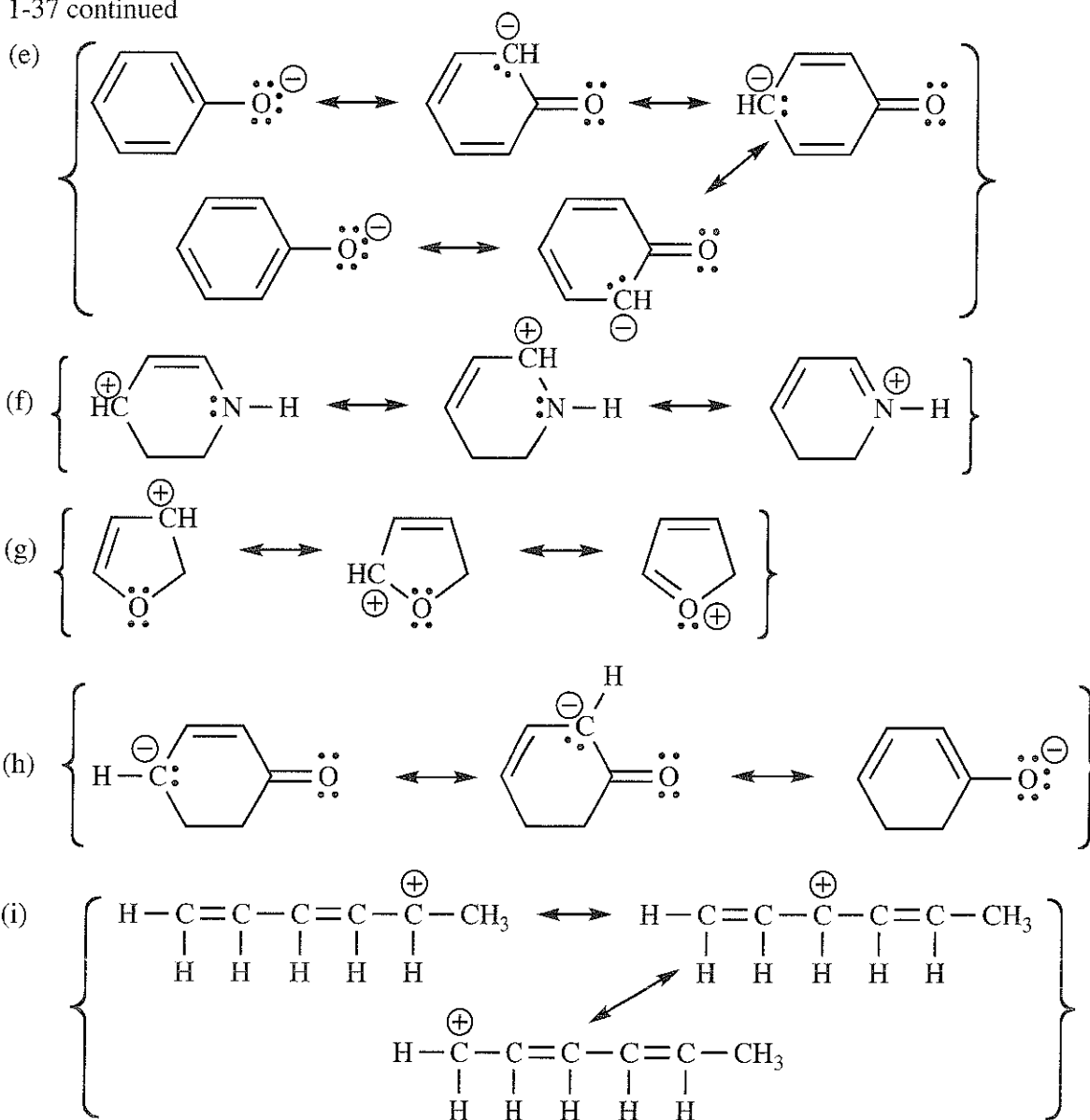
- (a) Different compounds—a hydrogen atom has changed position.
 (b) Resonance forms—only the position of electrons is different.
 (c) Different compounds—a hydrogen atom has changed position.
 (d) Resonance forms—only the position of electrons is different.
 (e) Different compounds—a hydrogen atom has changed position.
 (f) Resonance forms—only the position of electrons is different.
 (g) Resonance forms—only the position of electrons is different.
 (h) Different compounds—a hydrogen atom has changed position.
 (i) Resonance forms—only the position of electrons is different.
 (j) Resonance forms—only the position of electrons is different.

1-37



When drawing resonance forms with charges on ring atoms, it helps keep track by writing the C or N or O with the charge.

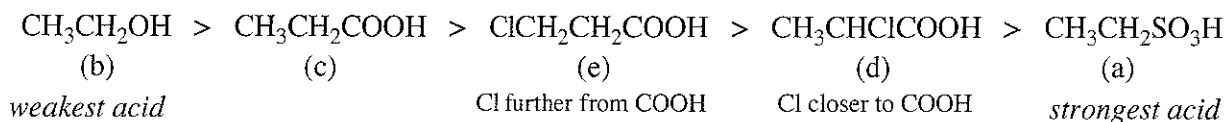
1-37 continued



(j) No resonance forms—the charge must be on an atom next to a double or triple bond, or next to a non-bonded pair of electrons, in order for resonance to delocalize the charge.

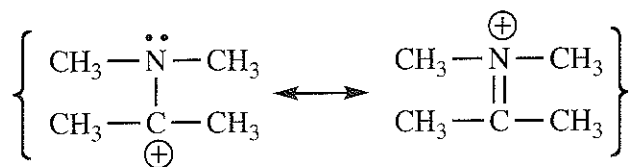
1-38 One of the fundamental principles of acidity is that the strength of the acid depends on the stability of the conjugate base. The two primary factors governing the strength of organic acids are resonance and inductive effects; of these two, resonance is usually the stronger and more important effect. For a more complete discussion, see Appendix 2 in this manual, especially section III.A.

Any organic structure with an $-\text{SO}_3\text{H}$ in it is a very strong acid because the anion has three significant resonance contributors; see the solution to 1-18(g). An organic structure with $-\text{COOH}$ is moderately strong since the conjugate base has two significant resonance contributors, also shown in the solution to 1-18(g). A structure with a simple $-\text{OH}$ does not have any resonance stabilization of the conjugate base, so it is the weakest acid. Within each group, inductive effects from an electronegative atom like Cl will have a small effect.

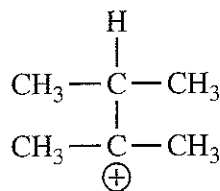


1-41 continued

(e)



more stable—resonance stabilized

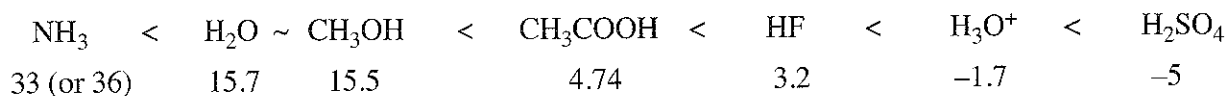


no resonance stabilization

1-42 These pK_a values from the text, Table 1-5 and Appendix 4, provide the answers. The lower the pK_a , the stronger the acid. Water and CH_3OH are very close.

least acidic

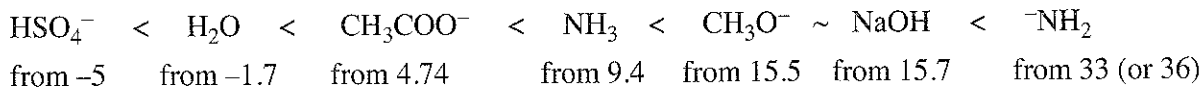
most acidic



1-43 Conjugate bases of the weakest acids will be the strongest bases. The pK_a values of the conjugate acids are listed here. (The relative order of some bases was determined from the pK_a values in Appendix 4 of the textbook.)

least basic

most basic



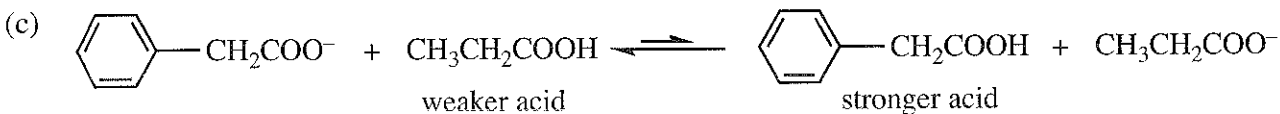
1-44

(a) $\text{pK}_a = -\log_{10} K_a = -\log_{10} (5.2 \times 10^{-5}) = 4.3$ for phenylacetic acid

for propionic acid, pK_a 4.87: $K_a = 10^{-4.87} = 1.35 \times 10^{-5}$

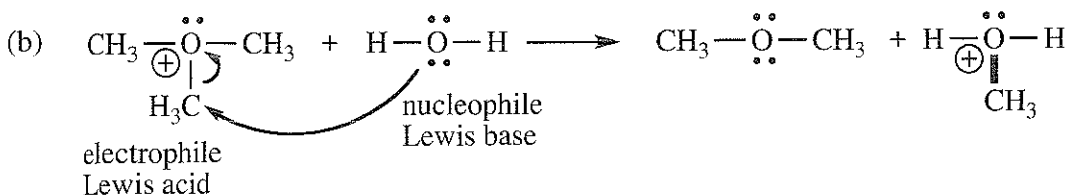
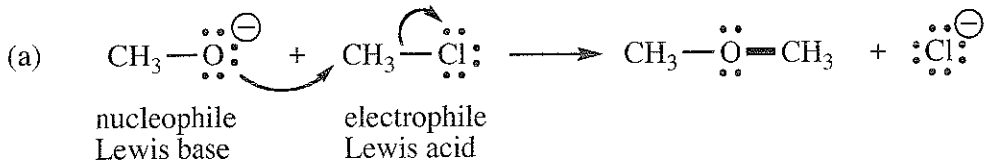
(b) Phenylacetic acid is 3.9 times stronger than propionic acid.

$$\frac{5.2 \times 10^{-5}}{1.35 \times 10^{-5}} = 3.9$$

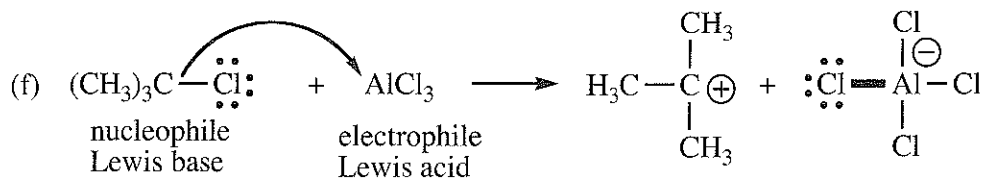
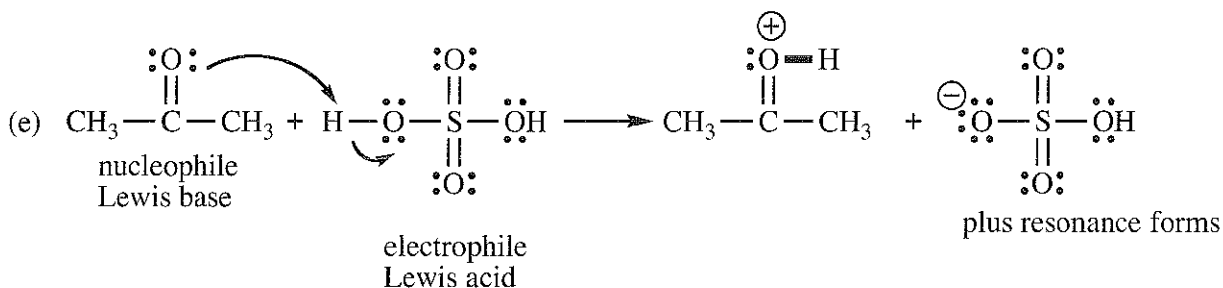
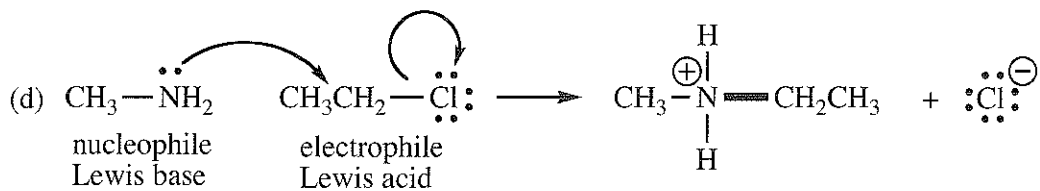
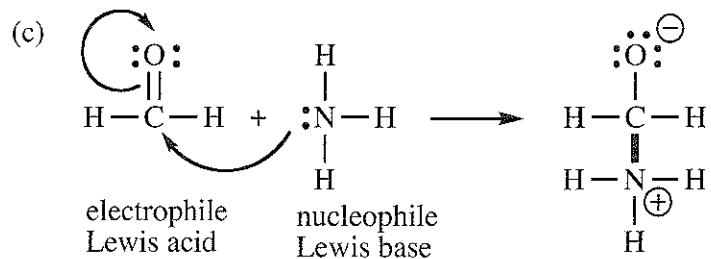


Equilibrium favors the weaker acid and base. In this reaction, **reactants** are favored.

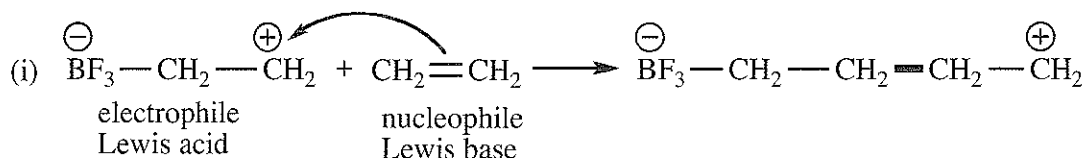
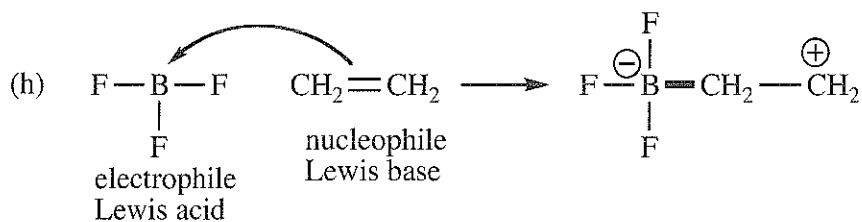
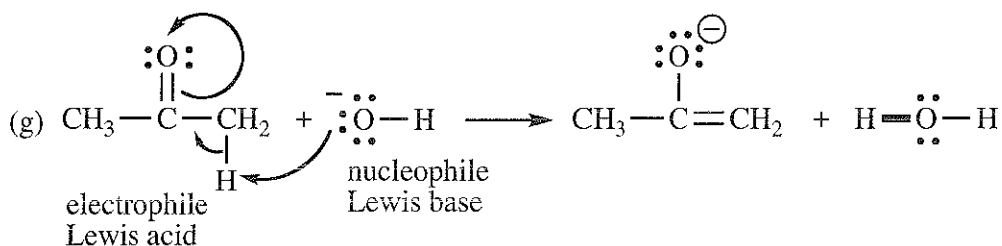
1-45 The newly formed bond is shown in bold.

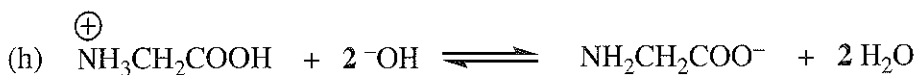
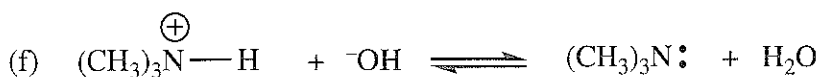
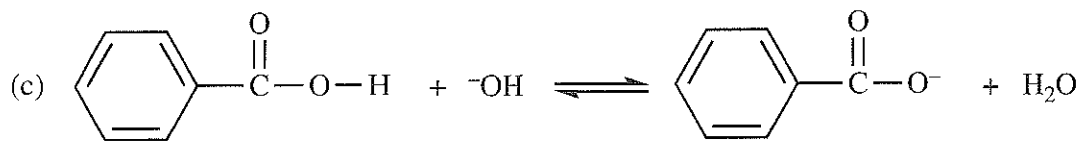


1-45 continued



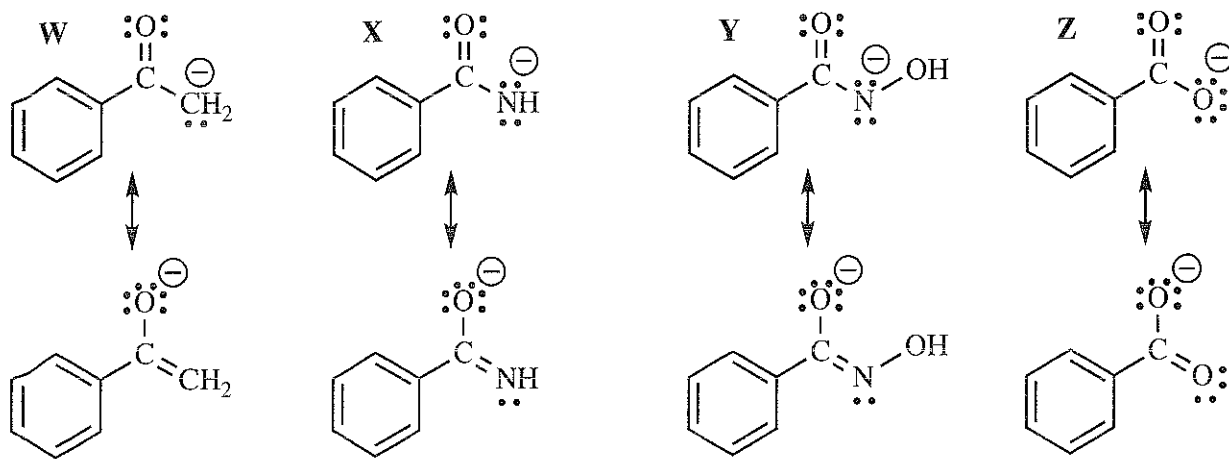
This may also be written in two steps: association of the Cl with Al, and a second step where the C-Cl bond breaks.





1-47 The critical principle: *the strength of an acid is determined by the stability of its conjugate base.*

(a) conjugate bases

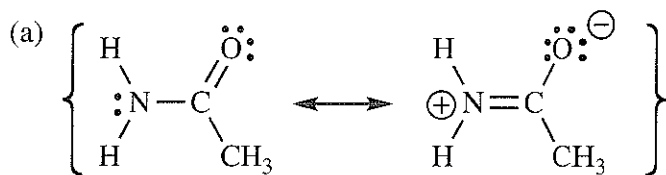


(b) **X** is a stronger acid than **W** because the more electronegative N in **X** can support the negative charge better than carbon, so the anion of **X** is more stable than the anion of **W**.

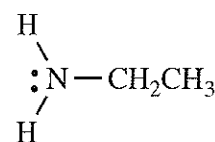
(c) **Y** is a stronger acid than **X** because the negative charge in **Y** is stabilized by the *inductive effect* from the electronegative oxygen substituent, the OH.

(d) **Z** is a stronger acid than **Y** because of two effects: O is more electronegative than N and can support the negative charge of the anion better, plus the anion of **Z** has two EQUIVALENT resonance forms which is particularly stable.

1-48 Basicity is a measure of the ability of an electron pair to form a new bond with H^+ of an acid. Availability of electrons is the key to basicity.

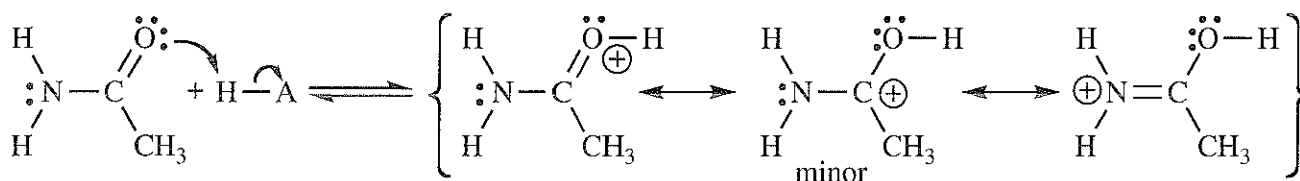
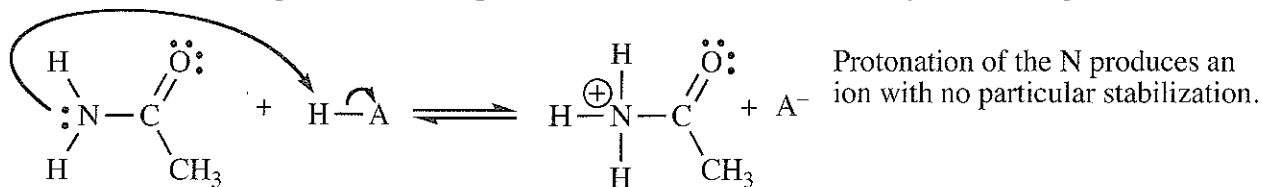


The electron pair in acetamide is *delocalized* over many atoms, not readily available for bonding with H^+ , making it a much weaker base than ethylamine.



The electron pair in ethylamine is *localized*, not distributed over many atoms. It is readily available for bonding with H^+ .

(b) Acetamide has two possible sites of protonation, the N and the O. HA symbolizes a generic acid.



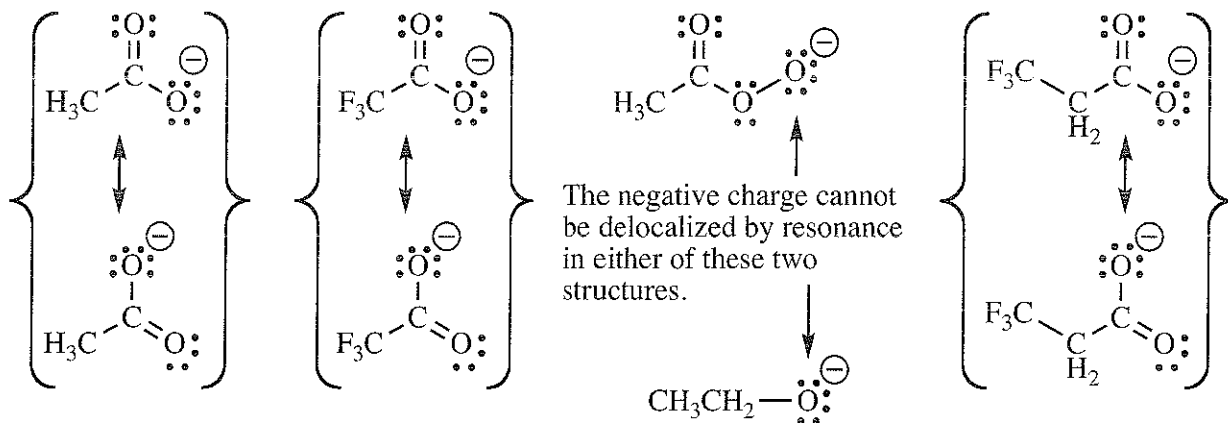
Protonation of the O produces an ion with *resonance stabilization*, a far more stable product than protonation on N. The O is the more basic atom in this structure.

1-49

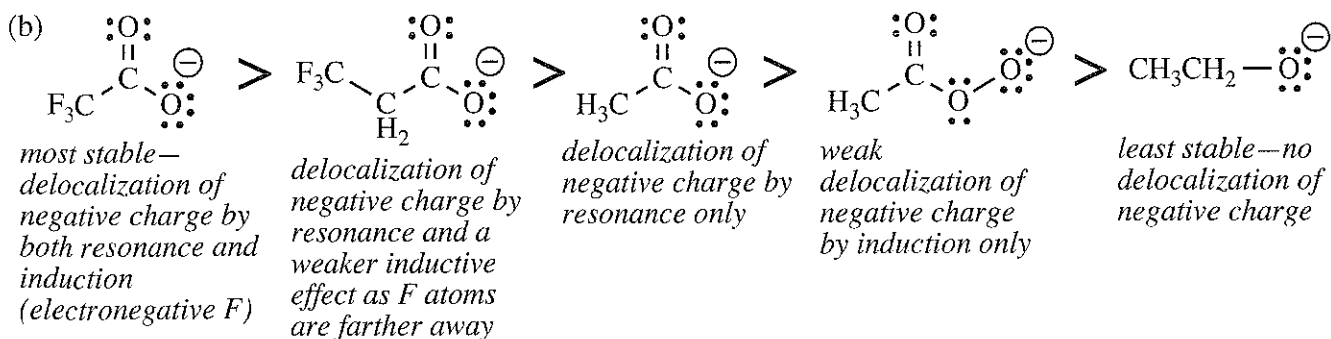


(b) The conjugate acid of CH_3Li is CH_4 . Table 1-5 gives the pK_a of CH_4 as > 40 , one of the weakest acids known. The conjugate base of one of the weakest acids known must be one of the strongest bases known.

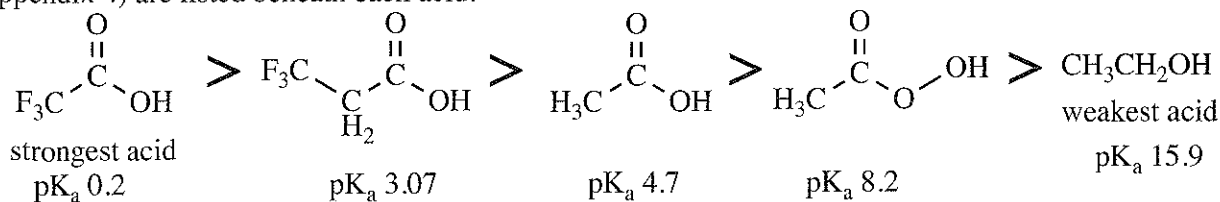
1-50 (a) conjugate bases



1-50 continued

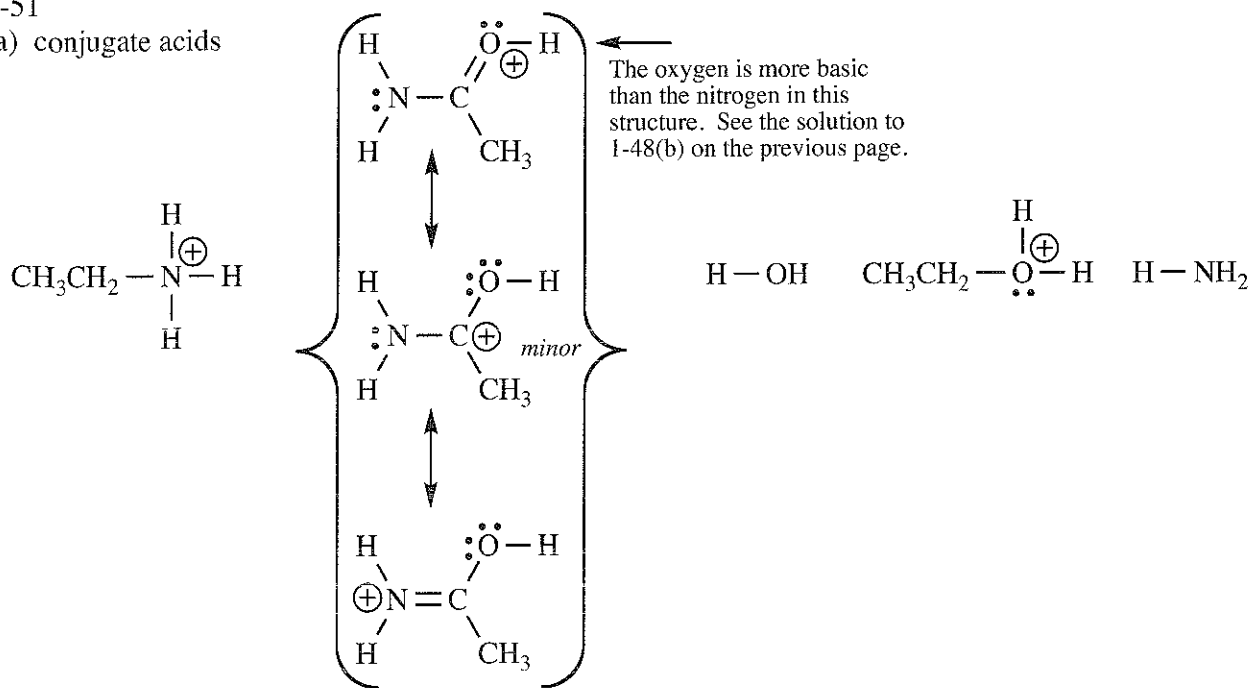


(c) The strongest acid will have the most stable conjugate base. The actual pK_a values (some from text Appendix 4) are listed beneath each acid.

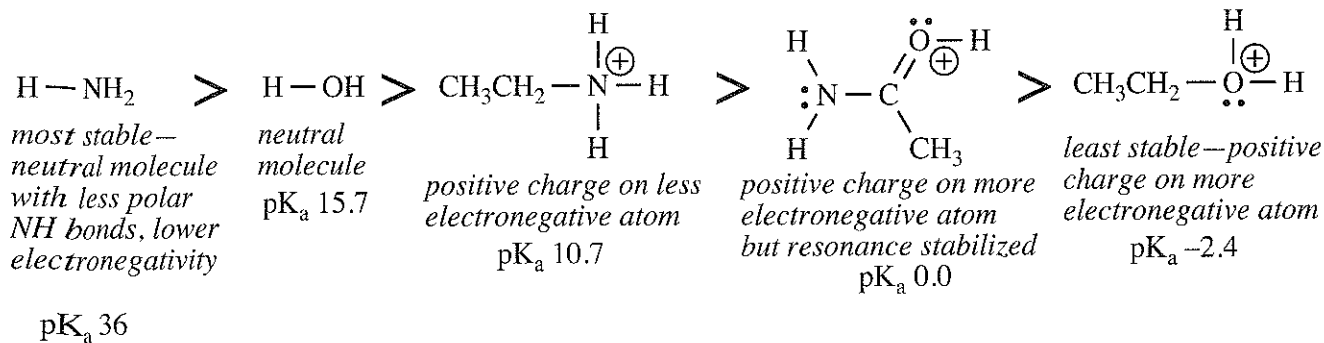


1-51

(a) conjugate acids

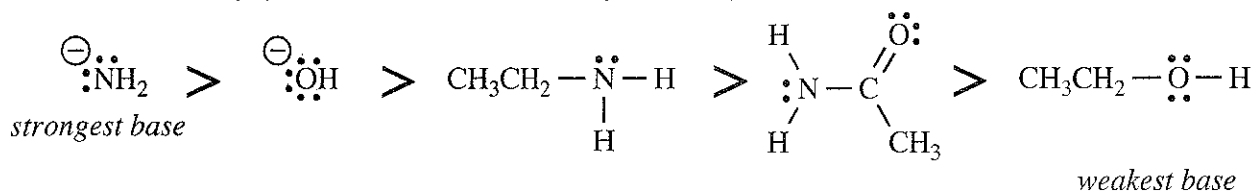


(b) order of decreasing stability (pK_a values from Appendix 4 in the text)

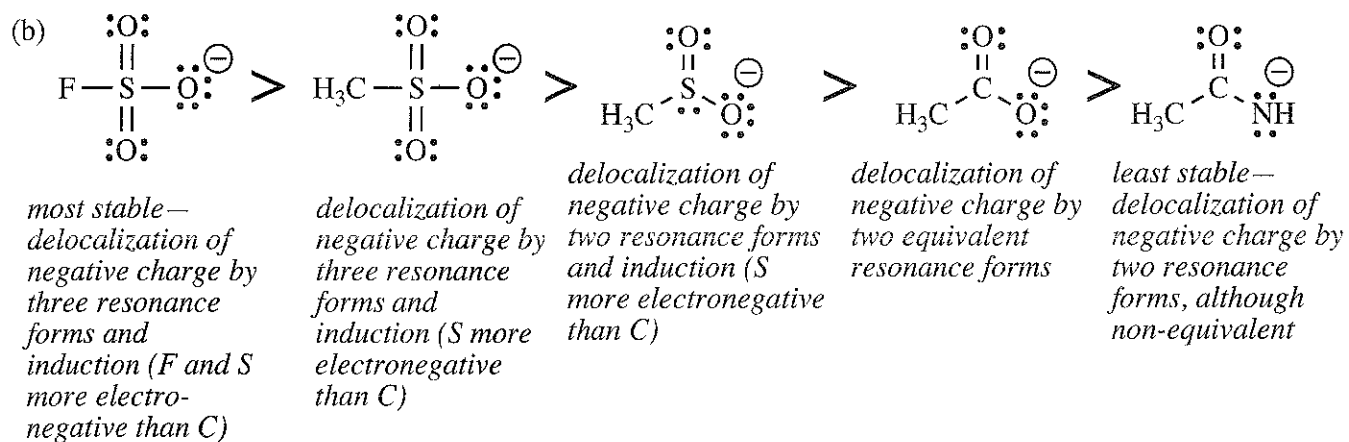
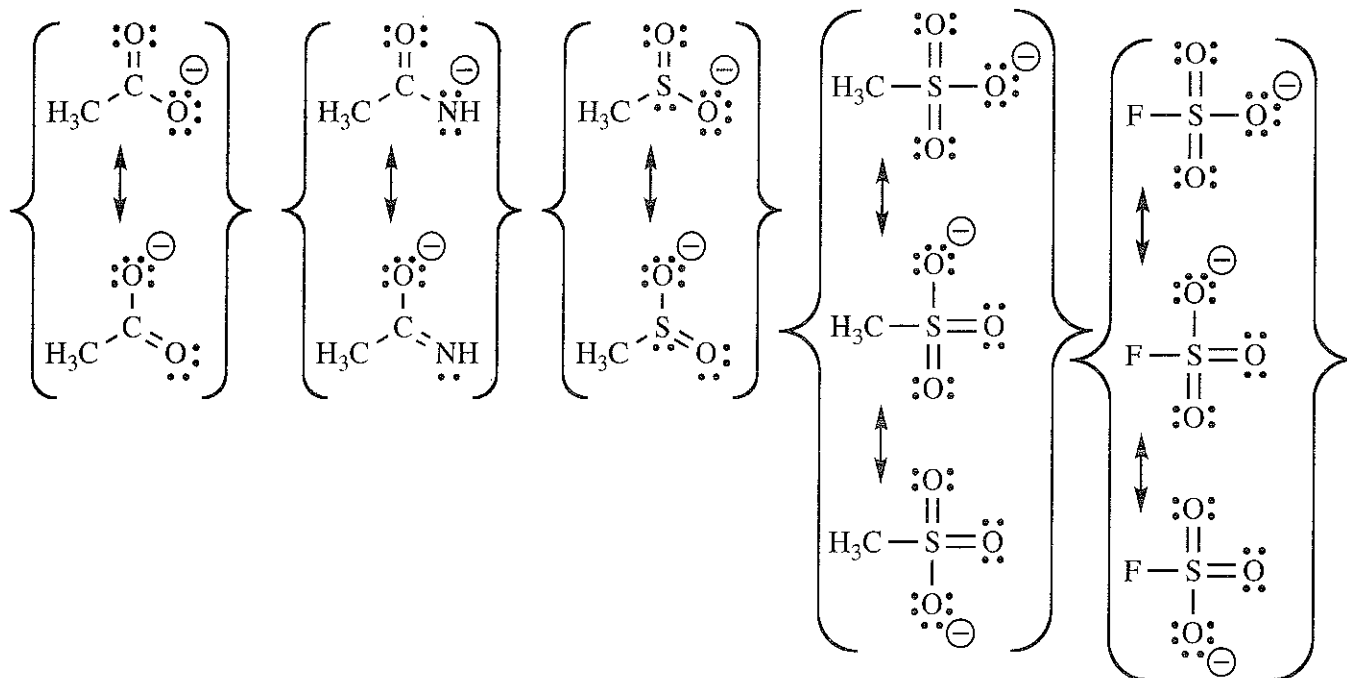


1-51 continued

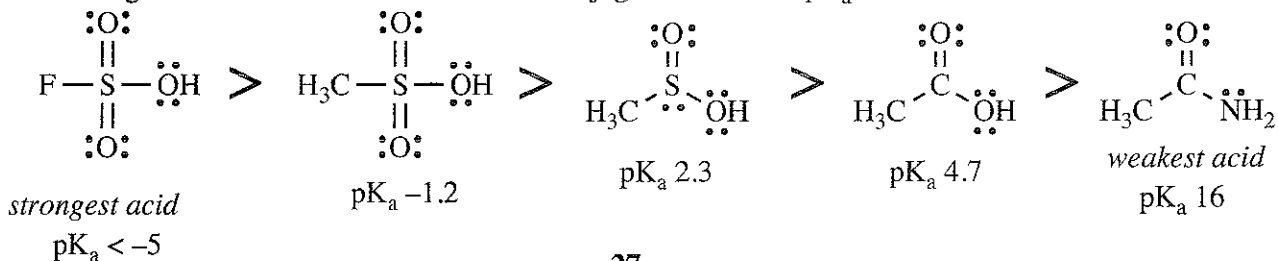
(c) The weakest conjugate acid will form the strongest conjugate base.



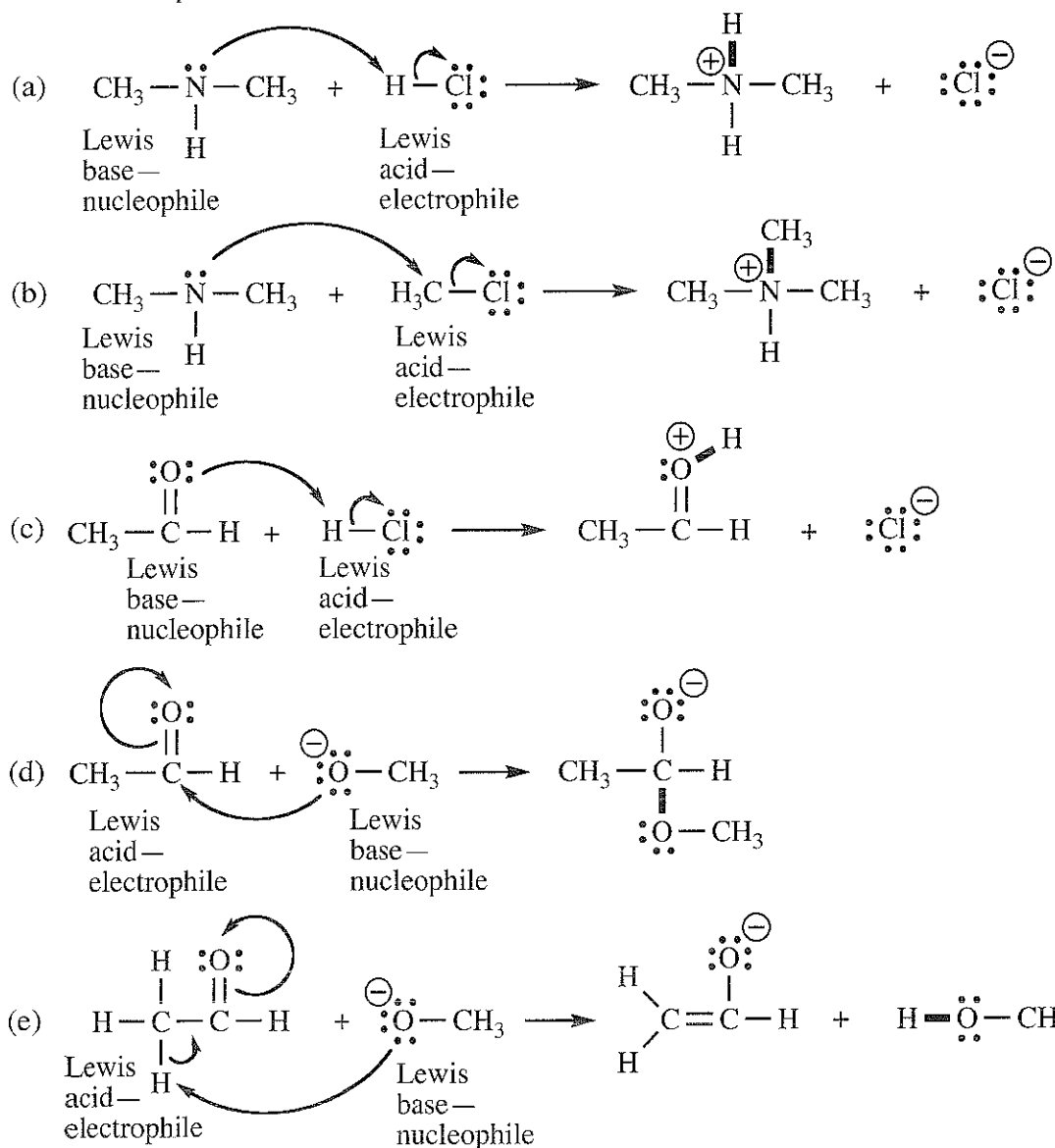
1-52 (a) conjugate bases



(c) The strongest acid will have the most stable conjugate base. The pK_a values are listed beneath each acid.



1-53 In each product, the new bond is shown in bold.



1-54 From the amounts of CO_2 and H_2O generated, the milligrams of C and H in the original sample can be determined, thus giving by difference the amount of oxygen in the 5.00-mg sample. From these values, the empirical formula and empirical weight can be calculated.

(a) how much carbon in 14.54 mg CO_2

$$14.54 \text{ mg } \text{CO}_2 \times \frac{1 \text{ mmole } \text{CO}_2}{44.01 \text{ mg } \text{CO}_2} \times \frac{1 \text{ mmole } \text{C}}{1 \text{ mmole } \text{CO}_2} \times \frac{12.01 \text{ mg } \text{C}}{1 \text{ mmole } \text{C}} = 3.968 \text{ mg } \text{C}$$

how much hydrogen in 3.97 mg H_2O

$$3.97 \text{ mg } \text{H}_2\text{O} \times \frac{1 \text{ mmole } \text{H}_2\text{O}}{18.016 \text{ mg } \text{H}_2\text{O}} \times \frac{2 \text{ mmoles } \text{H}}{1 \text{ mmole } \text{H}_2\text{O}} \times \frac{1.008 \text{ mg } \text{H}}{1 \text{ mmole } \text{H}} = 0.444 \text{ mg } \text{H}$$

how much oxygen in 5.00 mg estradiol

$$5.00 \text{ mg estradiol} - 3.968 \text{ mg } \text{C} - 0.444 \text{ mg } \text{H} = 0.59 \text{ mg } \text{O}$$

continued on next page

1-54 continued

calculate empirical formula

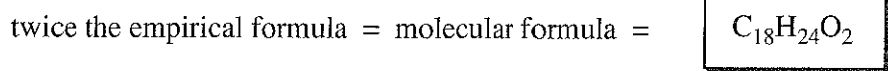
$$\frac{3.968 \text{ mg C}}{12.01 \text{ mg/mmole}} = 0.3304 \text{ mmoles C} \div 0.037 \text{ mmoles} = 8.93 \approx 9 \text{ C}$$

$$\frac{0.444 \text{ mg H}}{1.008 \text{ mg/mmole}} = 0.440 \text{ mmoles H} \div 0.037 \text{ mmoles} = 11.9 \approx 12 \text{ H}$$

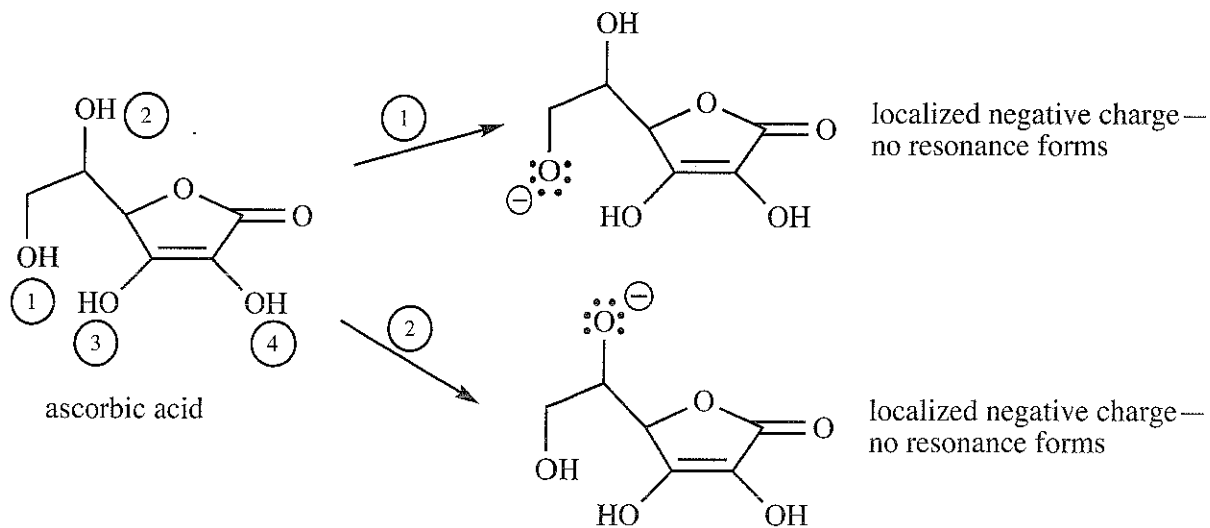
$$\frac{0.59 \text{ mg O}}{16.00 \text{ mg/mmole}} = 0.037 \text{ mmoles O} \div 0.037 \text{ mmoles} = 1 \text{ O}$$



(b) molecular weight = 272, exactly twice the empirical weight

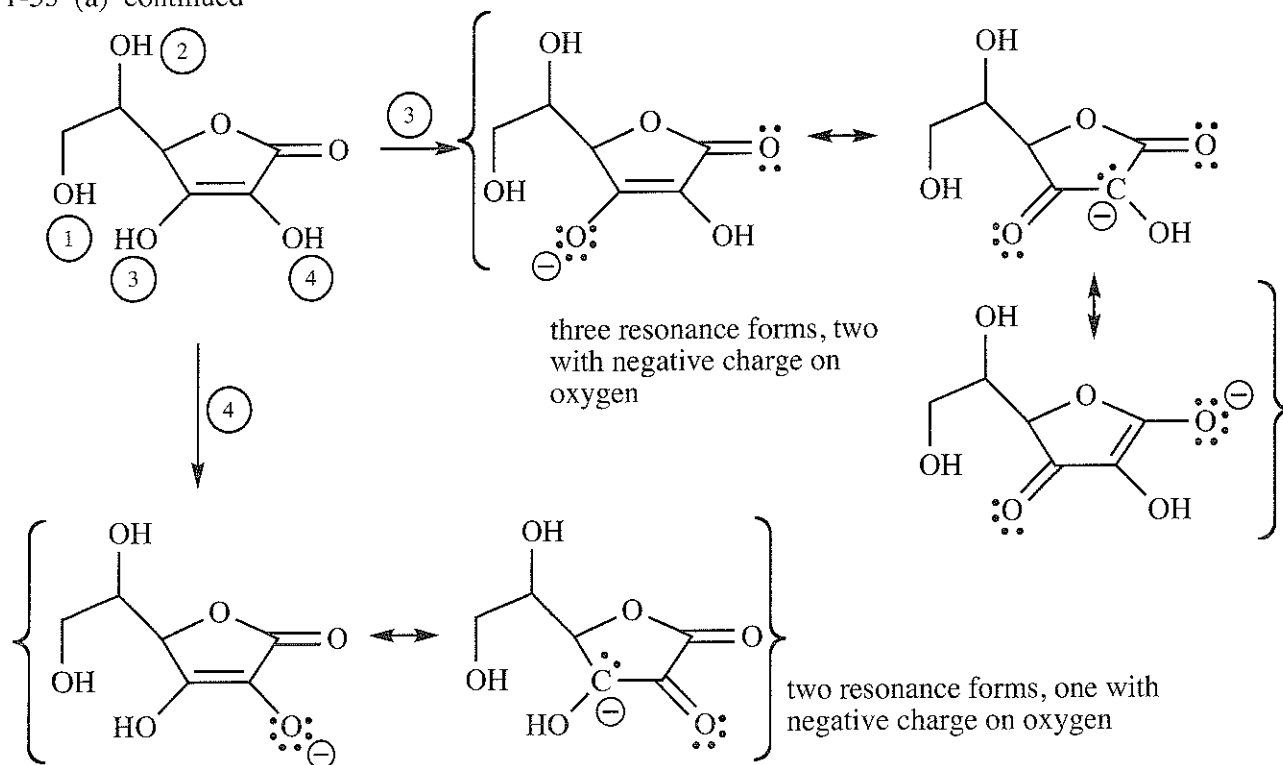


1-55 (a) Ascorbic acid has four OH groups that could act as acids. The ionization of each shows that one gives a more stable conjugate base.



continued on next page

1-55 (a) continued



(b) The ionization of the OH labeled "3" produces a conjugate base with three resonance forms, two of which have negative charge on oxygen. This OH is the most acidic group in ascorbic acid.

(c) The conjugate base of acetic acid, the acetate ion, CH_3COO^- , has two resonance forms (see the solution to problem 1-52(a), page 27 of this manual), each of which has a $\text{C}=\text{O}$ and a negatively charged oxygen, similar to two of the resonance forms of the ascorbate ion. The acidity of these two very different molecules is similar because the stabilization of the conjugate base is so similar. *The strength of an acid is determined by the stability of its conjugate base.*

Note to the student: Organic chemistry professors will ask you to "explain" questions, that is, to explain a certain trend in organic structures or behavior of an organic reaction. The professor is trying to determine two things: 1) does the student understand the principle underlying the behavior? 2) does the student understand how the principle applies in this particular example?

To answer an "explain" question, somewhere in your answer should be a statement of the principle, like: *"The strength of an acid is determined by the stability of its conjugate base."* From there, show through a series of logical steps how the principle applies, like drawing resonance forms to show which acid has the most stable conjugate base through resonance or induction. Answering these questions is like crossing a creek on stepping stones. Each phrase or sentence is a step to the next stone. When strung together, the steps bridge the gap between the principle and the observation.