3:   Haloalkanes, Alcohols, Ethers, and Amines

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•*Halogen, OH, and NH$_2$ Functional Groups*

•*Haloalkanes (RX)*

•*Alcohols (ROH)*

•*Ethers (ROR)*

•*Amines (RNH$_2$, R$_2$NH, R$_3$N)*

•*Amines are Organic Bases*

Preview

This chapter describes several classes of organic compounds with functional groups containing N, O, or halogen atoms (X) on their carbon skeletons. As a result, they have C-N, C-O, or C-X bonds (X = F, Cl, Br, or I) in addition to C-C and C-H bonds. These **haloalkanes** (RX), **alcohols** (ROH), **ethers** (ROR), and **amines** (RNH$_2$, R$_2$NH, R$_3$N) have different properties than alkanes and cycloalkanes because the X, O, and N atoms have *valence shell unshared electron pairs* and their bonds to C are *polar*. We will see that *amines* are **organic bases** because they react with both *weak* and *strong acids*. In order to discuss these acid/base reactions of amines, we review concepts of *acidity* and *basicity* in this chapter.

3.1 Halogen, OH, and NH$_2$ Functional Groups

Alkanes and cycloalkanes contain only C and H atoms, but most organic molecules also have other atoms such as N, O, and halogens (F, Cl, Br, and I). We will begin our study of these molecules by examining those containing *fluorine (F), chlorine (Cl), bromine (Br) or iodine (I)* (designated as *X*), as well as those with *OH* or *NH$_2$* groups. We write the general formulas of these compounds as *R-X*, *R-OH*, and *R-NH$_2$*.

Haloalkanes, Alcohols, and Amines (3.1A)

The general formulas *R-X*, *R-OH*, and *R-NH$_2$* suggest two different ways to view these classes of compounds. One way is for us to imagine that an alkyl group R replaces <u>H</u> in <u>H</u>-NH$_2$ (ammonia), <u>H</u>-OH (water), and the hydrogen halides <u>H</u>-X (X = F, Cl, Br, or I). We can also view haloalkanes (R-X), alcohols (R-OH), and amines (R-NH$_2$) as *alkanes* or *cycloalkanes* (*R-<u>H</u>*) where an X, OH, or NH$_2$ functional group replaces an <u>H</u>.

Simple Examples. The simplest examples of each of these classes are those where we replace an H of methane (CH$_4$) so that R is the methyl group CH$_3$. [graphic 3.1] In these new compounds C remains tetrahedral (Chapters 1 and 2), but we will see that its bond

3

3.1. Simplest Haloalkane, Alcohol and Amine

Haloalkane   Alcohol   Amine
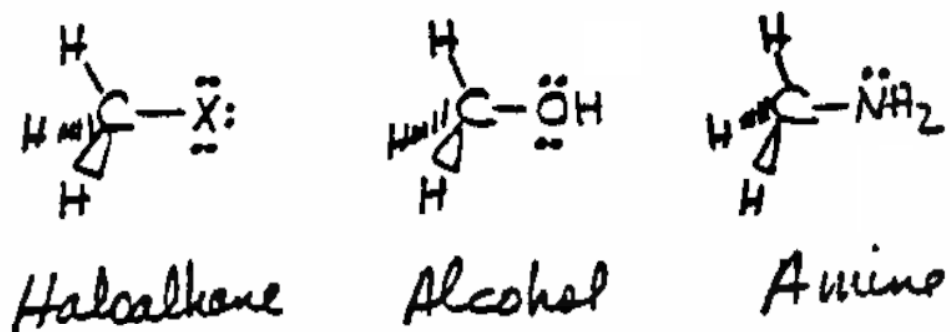
3.2. C-X, C-O, and C-N Bonds are Polar
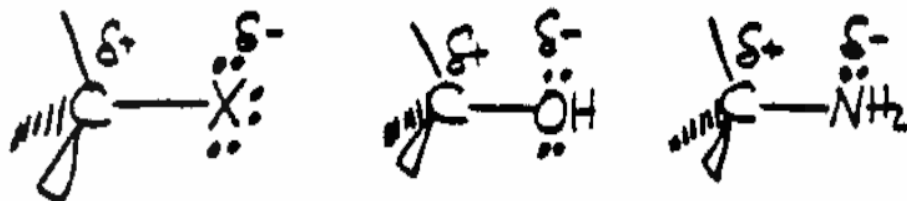
Figure [graphic 3.3]. A partial periodic table showing the first 10 elements, the remaining halogens, their preferred number of chemical bonds, and number of valence shell unshared electron pairs in their neutral compounds.

	H 1							He 2
	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9 Cl 17 Br 35 I 53	Ne 10
Bonds	1	2	3	4	3	2	1	0
Unshared e pairs	0	0	0	0	1	2	3	4

angles deviate from the ideal value of 109.5° to accommodate the different sizes of these functional groups.

Unsahared Electron Pairs and Polar Bonds. *R-X*, *R-OH*, and *R-NH$_2$* have different properties than alkanes or cycloalkanes (R-H) because their N, O, and X atoms have (1) **unshared pairs of electrons** in their outer valence electron shells , and (2) **polar** C-N, C-O, and C-X bonds. [graphic 3.2] In these *polar bonds*, C has a partial positive charge (δ^+) while the N, O, and X atoms have partial negative charges (δ^-). The *valence shell unshared electron pairs* are the pairs of dots on X, O, and N. Before we discuss these amines (R-NH$_2$), alcohols (R-OH), and haloalkanes (R-X), lets explore general properties of molecules that have atoms with *unshared electron pairs* and *polar chemical bonds*.

Unshared Electron Pairs (3.1B)

We learned in Chapter 1 about the regular patterns for the number of unshared electron pairs and the number of chemical bonds on atoms. These are shown again in Figure [graphic 3.3] for some atoms that we frequently find in organic compounds. [graphic 3.3]

Carbon, Nitrogen, Oxygen, and Fluorine. The compounds $\underline{C}H_4$, $\underline{N}H_3$, $H_2\underline{O}$, and $H\underline{F}$, illustrate these patterns of bonds and unshared electron pairs for C, N, O, and F. [graphic 3.4] The number of *bonds* decreases in the order 4 (C), 3 (N), 2 (O), 1 (F), while the number of *unshared electron pairs* in their outer valence shells increases in the order 0 (C), 1 (N), 2 (O), 3 (F). As a result, the sum of the number of *chemical bonds* and *valence shell unshared electron pairs* is 4 for each of these atoms. Since there are two electrons in each bond, and in each unshared electron pair, the total number of electrons in bonds and unshared electron pairs is 8 for C, N, O, and F in these compounds. The same is true in their organic compounds R-F, R-OH, and R-NH$_2$.

Chlorine, Bromine, and Iodine. While some atoms in the third and higher rows of the periodic table form compounds with more than 8 outer valence shell electrons, Cl, Br, and I (Figure [graphic 3.3]) have the same valence shell electron configurations as F. They each have three unshared electron pairs and one chemical bond in haloalkanes (R-X). [graphic 3.5]

Hydrogen. The outer valence shell of H can have only two electrons because it is in the first row of the periodic table. As a result, it forms only one chemical bond and has no unshared electrons (Figure [graphic 3.3]).

3.4
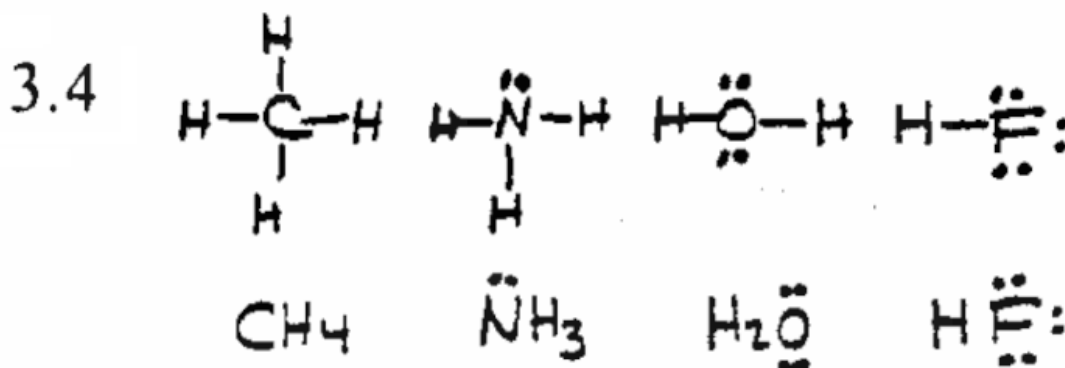
	CH₄	NH₃	H₂O	HF
Bonds	4	3	2	1
Unshared e pairs	0	1	2	3

3.5. Halogen Atoms have Three Unshared Electron Pairs

H–F: H–Cl: H–Br: H–I:

Often represented as H–X:
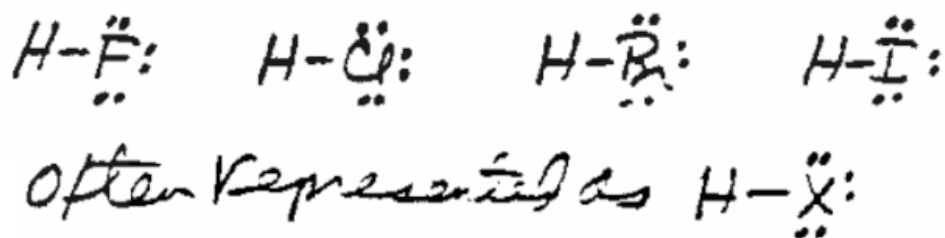
3.6
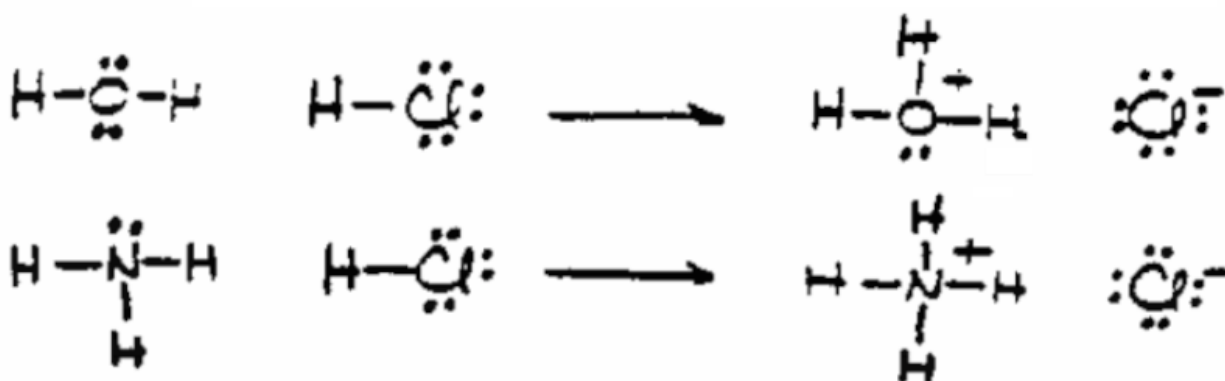
Chemical Reactivity of Unshared Electron Pairs. Unshared electron pairs are chemically reactive and can participate in chemical bond formation. For example, we will see later in this chapter that both H_2O and NH_3 use an unshared electron pair on O or N to accept an H^+ from an acid to form an additional O-H or N-H bond. [graphic 3.6]   These **protonation** reactions also occur with unshared electron pairs on N and O in $R-NH_2$, R-OH, and other compounds with these atoms, as we will show later in this chapter.

Bond Polarity (3.1C)

With the exception of the *protonated* amines and alcohols just mentioned, all of the organic molecules that we have considered have no ionic charge so they are **electrically neutral**. A molecule is *electrically neutral* because the total number of its electrons (-1 charge) is equal to the number of protons (+1 charge) in its atomic nuclei. However while *electrically neutral* molecules have no electrical charge, many of them such as haloalkanes (R-X), alcohols (R-OH), and amines ($R-NH_2$) have **polar bonds**. [graphic 3.7]

*Electron Distribution in Polar Bonds*. Chemical bonds are polar when the electron distribution in their bonding molecular orbital is not symmetrically distributed between the two bonded atoms. [graphic 3.8]   Both CH_4 and CH_3F are electrically neutral molecules, but CH_3F has a polar C-F bond, while CH_4 has no polar bonds. Electron pairs in the C-H bonds of CH_4 are distributed in their bonding MO's so that they interact to about the same extent with both the C and H nuclei (Figure [graphic 3.8]). In contrast, a C-F bonding electron pair is unsymmetrically distributed in its bonding MO so that it interacts to a much greater extent with F than with C. As a result, the C of a C-F bond is somewhat electron deficient (δ^+) while the F has an excess of electron density (δ^-) and the bond is polarized (δ^+)C-F(δ^-). The same type of asymmetric electron distribution occurs with C-Cl, C-Br, C-O, and C-N bonds.

Electronegativity. The **electronegativity** values of atoms (Figure [graphic 3.9]) reflect the relative ability of two bonded atoms to attract the electron pair in their bond. [graphic 3.9]   The resultant polarity of these bonds depends on the difference in electronegativity of the bonded atoms (Table 3.1).

Table 3.1. Electronegativity Differences for Bonded Atoms

Bonded Atoms	Electronegativity Difference*
C-F	+1.4
C-Cl	+0.6
C-Br	+0.5
C-I	+0.2
C-O	+0.9
C-N	+0.4
C-H	-0.2

*(Electronegativity of Atom - Electronegativity of C)

3.7. Neutral Molecules with Polar Bonds

$H_3C - \ddot{\underset{..}{X}}:$ has a Polar C–X bond $H_3\overset{\delta\oplus}{C} - \overset{\delta\ominus}{\ddot{\underset{..}{X}}}:$

$H_3C - \ddot{\underset{..}{O}}H$ has a Polar C–O bond $H_3\overset{\delta\oplus}{C} - \overset{\delta\ominus}{\ddot{\underset{..}{O}}}H$

$H_3C - \ddot{N}H_2$ has a Polar C–N bond $H_3\overset{\delta\oplus}{C} - \overset{\delta\ominus}{\ddot{N}}H_2$
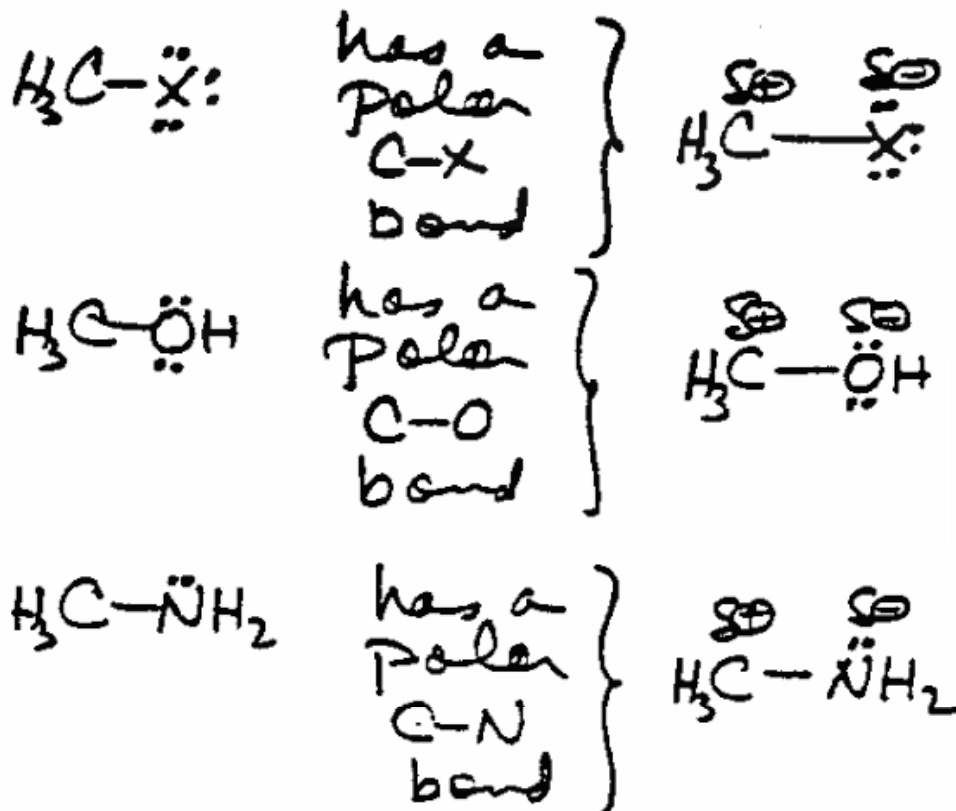
3.8. "Electron Cloud" Pictures of Chemical Bonds
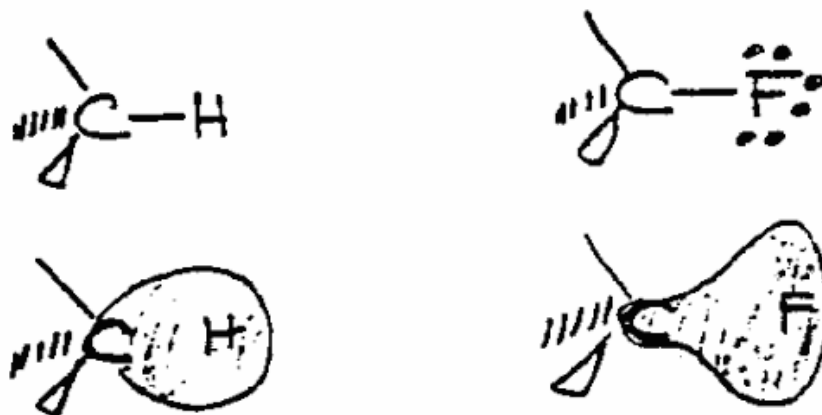
H
2.3

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	2.9	3.4	3.9

Na	Mg	Al	Si	P	S	Cl
0.9	1.4	1.8	2.3	2.3	2.7	3.1

Br
3.0

Figure [graphic 3.9] . Electronegativity values for selected elements in the periodic table. These are Mulliken values converted to the Pauling scale (Bratsch, S. G. *J. Chem. Ed.* **1988**, *65*, 34, and 223)

I
2.7

-

3.10. C-F Bond Dipoles
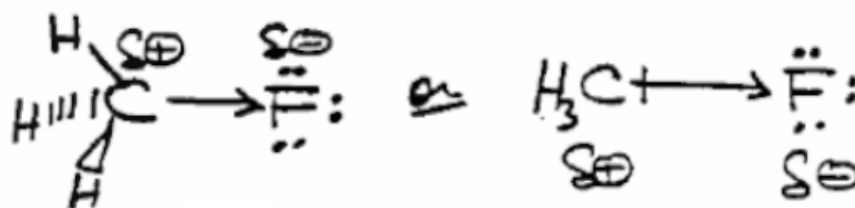
3.11. Molecular Dipole in CH_3F
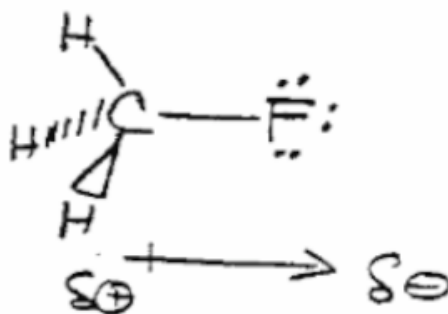
F attracts electrons more than C in C-F bonds because the electronegativity of F (3.9) is much greater than that of C (2.5). In contrast, C-H bonds are not very polar because the electronegativities of H (2.3) and C (2.5) are about the same. *Positive* (+) values for the electronegativity differences in Table 3.1 mean that C is positively polarized (δ^+) while its attached atom is negatively polarized (δ^-).

The relative magnitudes of these electronegativity differences reflect the relative magnitudes of the polarity of each bond. The *negative* (-) electronegativity difference for a C-H bond suggests that C is (δ^-) while H is (δ^+), however the magnitude of the electronegativity difference is so small that we generally think of C-H bonds as nonpolar. (The electronegativity difference for a C-I bond is also small so it is relatively nonpolar compared to other C-X bonds. However an iodine atom (I) in a C-I bond is highly **polarizable** and we will see that it often acts as if it has weak $\delta(-)$ character.)
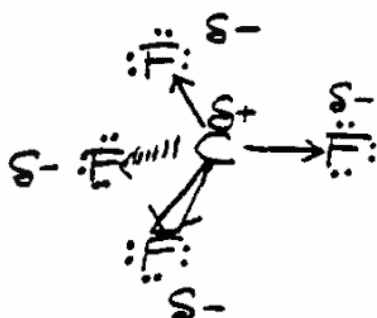
   Dipoles and Dipole Moments. *Polar bonds* (Table 3.1) have **bond dipoles** illustrated here for the C-F bond in CH_3F. [graphic 3.10]   The arrow represents the *bond dipole* and the arrowhead points toward the negative atom. The positive end of the dipole often has a "cross mark" representing a (+) sign. Bond dipoles can cause a molecule to have a **molecular dipole** where one "end" of the molecule is partially positive (δ^+) and the other end is partially negative (δ^-). [graphic 3.11] However, polar bonds do not always result in molecular dipoles. All four C-F bonds in CF_4 are polar with bond dipoles, but because they point toward the four corners of a tetrahedron (Figure [graphic 3.12]), their bond dipoles cancel each other and the molecule has no molecular dipole. [graphic 3.12]

The **dipole moment** of a molecule quantitatively describes the magnitude of its *molecular dipole*. It is much more important for you to recognize that a molecule has a molecular dipole, and to know which ends are negative and positive, than to know the specific value of its *dipole moment*.

3.2 Haloalkanes (R-X)

Now that we have learned about some general characteristics of molecules containing atoms with unshared electron pairs and polar bonds, let's begin our detailed examination of these compounds with the *haloalkanes* (*R-X*). While we can picture R-X molecules as organic derivatives of hydrogen halides (H-X), their chemical and physical properties suggest that it is better for us to view them as alkanes (R-H) substituted by halogen atoms (X).

3.12

Bond

These Dipoles Cancel Each Other
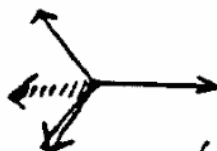
The Net Molecular Dipole Moment is Zero

3.13

$CH_3-\ddot{C}\ddot{l}:$

Chloromethane

$CH_3-CH_2-\ddot{C}\ddot{l}:$

Chloroethane

$CH_3-\underset{\overset{|}{:}\overset{..}{\underset{..}{F}}:}{CH}-CH_3$

2-Fluoropropane

$CH_3-CH-\underset{\overset{|}{CH_3}}{\overset{:\ddot{B}r:}{CH}}-CH_3$
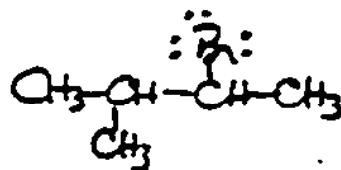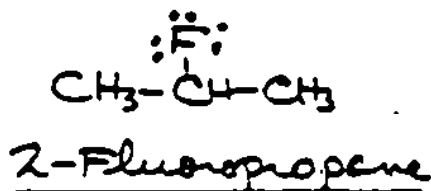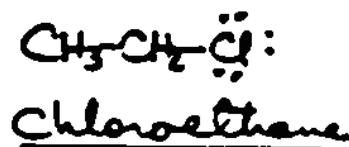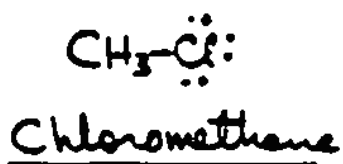
2-Bromo-3-Methylbutane

$CH_3-CH_2-\underset{\overset{|}{:\ddot{C}l:}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$
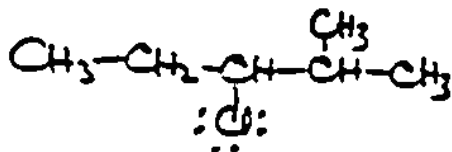
3-Chloro-2-Methylpentane

Iodocyclohexane

1-Ethyl-1-Iodocyclohexane

Cis-1-Bromo-2-ChloroCyclo-Pentane

11

Nomenclature (3.2A)

We systematically name *haloalkanes* and *halocycloalkanes* using nomenclature rules we learned for branched alkanes and cycloalkanes in Chapter 2.

Halogens are Substituents. We treat a halogen atom (X) as a *substituent* attached to a parent alkane or cycloalkane. As such, we place the number of the carbon to which it is attached and its name (Table 3.2) in front of the name of the parent alkane or cycloalkane, in alphabetical order, along with those of any alkyl substituents. [graphic 3.13]

Table 3.2. Names of The Halogen Substituents

Halogen Atom (X)	Substituent Name
F	fluoro
Cl	chloro
Br	bromo
I	iodo

Common Nomenclature. While it is easy to name haloalkanes using *systematic nomenclature*, organic chemists frequently refer to haloalkanes with simple alkyl groups by "*alkyl halide*" *common* names. [graphic 3.14] **Polyhalomethanes** such as CH_2X_2, CHX_3, and CX_4 also have a unique set of common names. [graphic 3.15]   Organic chemists use the systematic name *dichloromethane* and common name *methylene chloride* interchangeably for CH_2Cl_2, but they always refer to $CHCl_3$ and CCl_4 by their common names *chloroform* and *carbon tetrachloride*. *Polyfluoromethanes*, *polybromomethanes*, and *polyiodomethanes* have common names analogous to *polychloromethanes*, however we use systematic names when the carbon has two different halogens (*e.g.,* $BrCH_2Cl$ is bromochloromethane).

Freons. The polyhalogenated molecule CCl_3F is *trichlorofluoromethane*, but it also goes by the name "Freon-11" in industrial applications. **Freon** is a commercial trademark of the E. I. du Pont Company used to name a variety of fluorohaloalkanes such as the examples included in Table 3.2a.

Table 3.2a. Some Freons

Freon "Name"	Chemical Structure
Freon 11	CCl_3F
Freon 12	CCl_2F_2
Freon 113	CCl_3-CF_3
Freon 114	$CClF_2-CClF_2$
Freon 13B1	$CBrF_3$
Freon 1211	$CBrClF_2$

Freons have had a variety of important industrial uses as coolants in air conditioning and refrigeration systems, as the gaseous propellants in aerosol containers, and as the chemical agent in non-aqueous fire

12

3.14. Common Names of Simple Haloalkanes

Chloromethane

$CH_3-\ddot{\underset{..}{C}l}:$
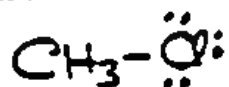
(Methyl Chloride)

Iodocyclohexane

$\ddot{\underset{..}{I}}:$

(Cyclohexyl iodide)

2-Bromopropane

$\overset{:\ddot{Br}:}{CH_3-CH-CH_3}$
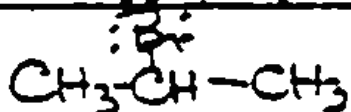
(Isopropyl bromide)

2-Fluoro-2-Methyl-
Propene

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\ddot{\underset{..}{F}}:$
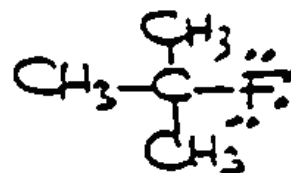
(t-Butyl fluoride)

3.15. Common Names of Polychloromethanes
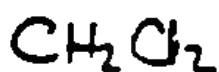
CH_2Cl_2　　Dichloromethane
　　　　　　　　or
　　　　Methylene Chloride
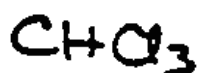
$CHCl_3$　　Trichloromethane
　　　　　　　or
　　　　Chloroform

CCl_4　　Tetrachloromethane
　　　　　　　or
　　　　Carbon Tetrachloride

extinguishers. However, many of them decompose in the earth's upper atmosphere and can cause depletion of the ozone layer. As a result, aerosol containers in the United States no longer contain Freons. While still used in other applications, certain Freons previously used in refrigeration and air conditioning systems are being replaced with other Freons that decompose in the lower atmosphere before reaching the ozone layer.

Properties of Haloalkanes (3.2B)

The properties of haloalkanes depend on their halogen atom.

Polarity and Dipole Moments. Polar C-X bonds cause most haloalkanes to have molecular dipoles and the magnitude of their dipole moments (Table 3.3) depend on X.

Table 3.3 Dipole Moments for Some Simple Haloalkanes

Haloalkane	Dipole Moment, (D)*
$CHCl_3$	1.02
CHF_3	1.60
CH_2Br_2	1.43
CH_2Cl_2	1.54
CH_2F_2	1.93
CH_3I	1.60
CH_3Br	1.80
CH_3Cl	1.87
CH_3F	1.81

*A dipole moment measures the amount of charge and the distance of its separation. The unit **D** (**debye**), named after the Dutch physicist Peter J. Debye (1884-1966), is equal to a charge of 3.33×10^{-30} coulombs separated by exactly 1 meter.

Since electronegativity values of X increase in the order I<Br< Cl <F (Figure [graphic 3.9] and Table 3.1) you might expect haloalkane dipole moments to also increase in this order. While this is true for dipole moments of trihaloalkanes (CHX_3) and dihaloalkanes (CH_2X_2), you can see that it is not generally true for monohaloalkanes (CH_3X) (Table 3.3).

As we would expect, the dipole moment for CH_3I has the lowest value, but those for CH_3F, CH_3Cl, and CH_3Br are all about the same even though the electronegativity values of F, Cl, and Br are quite different from each other. This inconsistency occurs because dipole moments depend not only on the <u>amount</u> of charge separated at the two ends of the dipole, but also the <u>distance</u> of that separation. The **bond lengths** of the C-X bonds determine the

distance of this charge separation and we will see below that these *bond lengths* are significantly different for the four halogens.

C-X Bond Length and Size of X. C-X *bond lengths* increase in the order C-F < C-Cl < C-Br < C-I (Table 3.4) because the size of X increases in the same order. The relative sizes of atoms in the same column of the periodic table depend on the number of electrons around each atom. Since F, Cl, Br, and I have 9, 17, 35, and 53 electrons, respectively, their relative sizes are F < Cl < Br < I.

Table 3.4. Approximate Bond Length Values for the C-X Bond in CH_3-X.

C-X Bond	C-X Bond Length, (Å)*
C-F	1.4
C-Cl	1.8
C-Br	2.0
C-I	2.2
C-H	1.1
C-CH_3	1.5

*Chemical bonds lengths range from about 1×10^{-8} cm (1 Å) to more than 2×10^{-8} cm (2 Å). The unit **Å** (**angstrom**), named after the Swedish physicist A. J. Ångström (1814-1874), is exactly 10^{-8} cm.

An Approximate Comparison of C-X Bond Polarities. Bond dipole moments (Table 3.3) depend both on *bond length* and the *amount of charge* separated. As a result, the decrease in C-X bond lengths from C-I to C-F offsets a simultaneous increase in amount of charge separated in C-X bonds leading to the relatively constant dipole moments seen for CH_3-X (Table 3.3). Actual calculations are complex, but you can get a qualitative idea of the relative polarities of the various C-X bonds by dividing the dipole moments for CH_3-X (Table 3.3) by the appropriate C-X bond lengths (Table 3.4).

The dipole moments of the CH_2X_2 and CHX_3 molecules are also affected by the C-X bond lengths, but the presence of more than one C-X bond in each of these systems causes the amount of overall charge separation in these molecules to more than compensate for the C-X bond length effect that we see in the CH_3X molecules.

Apparent Sizes of X. The relative sizes of halogen atoms (F < Cl < Br < I) are approximately reflected in the magnitudes of the CH_3-C-X bond angles in haloalkanes of the structure $(CH_3)_3$C-X (Table 3.5). You can see that increases in the CH_3-C-X bond angles with increasing halogen size leads to corresponding decreases in the CH_3-C-CH_3 angles. [graphic 3.16]

Table 3.5. Some "Tetrahedral" Angles for Different X Groups in $(CH_3)_3C-X$
Bond Angle (° (degrees))*

X	CH_3-C-X	CH_3-C-CH_3
F	106.6	112.2
Cl	107.4	111.5
Br	107.4	111.5
I	108.1	110.8

*These bond angles were measured in "calculated" molecular structures obtained with Spartan 3.1 software (Wavefunction, Inc.) on Silicon Graphics computers.

In contrast, the relative order of halogen size (F<Cl<Br<I) is much less apparent in their *equatorial preferences* (Chapter 2) (Table 3.6). [graphic 3.17]   We have seen that *equatorial preferences* reflect the relative sizes of *alkyl groups* substituted on cyclohexane. While they also indicate that all halogens are larger than H, and F is smaller than the other halogens, the equatorial preferences for Cl, Br, and I are all about the same in spite of their different sizes.

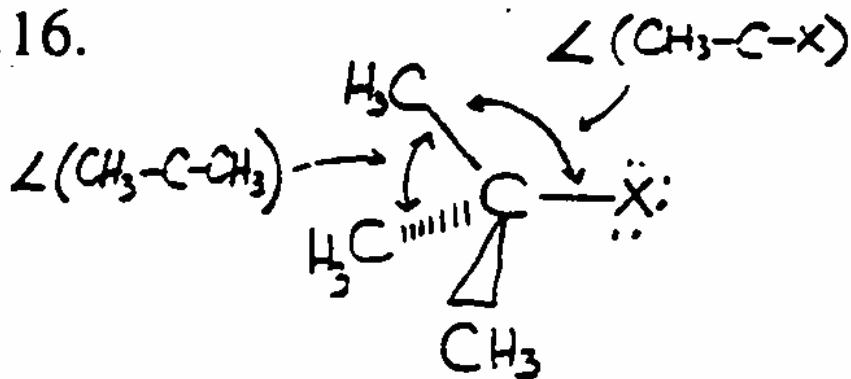**Table 3.6. Approximate Equatorial Preferences for Halogens and CH_3**

X	Equatorial Preference (kJ/mol)	%Equatorial Conformation
H	0.0	50
F	1.1 to 1.8 (1.5)*	61 to 67 (64)*
Cl	2.2 to 2.7 (2.5)	71 to 75 (73)
Br	2.0 to 2.8 (2.4)	69 to 76 (73)
I	2.0 to 2.6 (2.3)	69 to 74 (72)
CH_3	7.3	95.0
CH_3CH_2	7.5	95.4
$(CH_3)_2CH$	9.3	97.7
$(CH_3)_3C$	20	>99.9

()* are average values

This apparent inconsistency occurs because *equatorial preferences* measure different types of interactions than those that determine X-C-CH_3 *bond angles* (Table 3.5) or C-X *bond lengths* (Table 3.4). The equatorial preferences for X depend not only on the atomic radius of X, but also on the C-X bond length. As the C-X bond length increases, the halogen moves further away from neighboring atoms with which it sterically interacts. [graphic 3.18]   Since both the bond length and the size of X increase in the order F < Cl < Br < I, these two properties compensate leading to relatively constant equatorial preferences for Cl, Br, and I. (The identical CH_3-C-X bond angles for Cl and Br (Table 3.5) also probably result from a compensation between size of X and C-X bond length).

16

3.16.

3.17

Equatorial X
More Stable

Axial X
Less Stable

3.18

Separation About
The Same

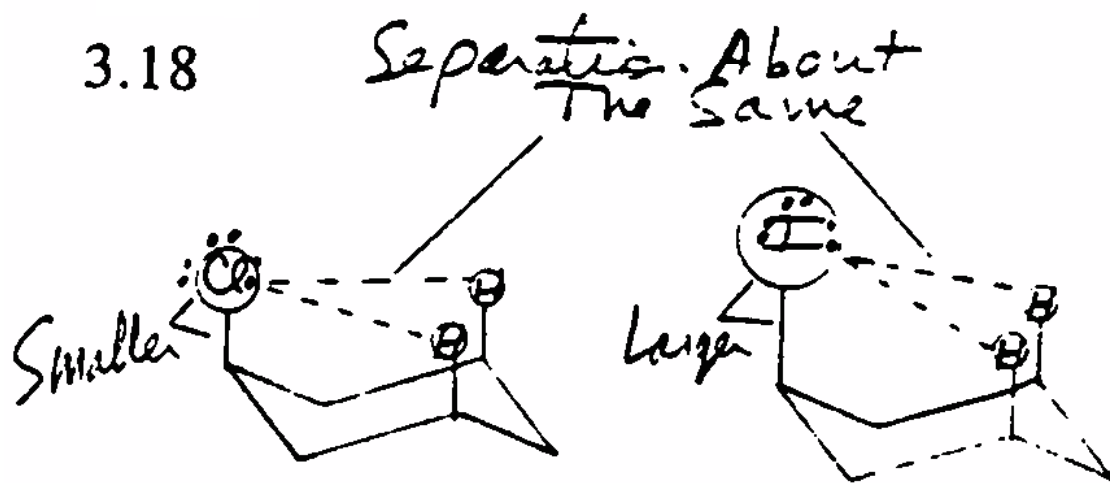Smaller
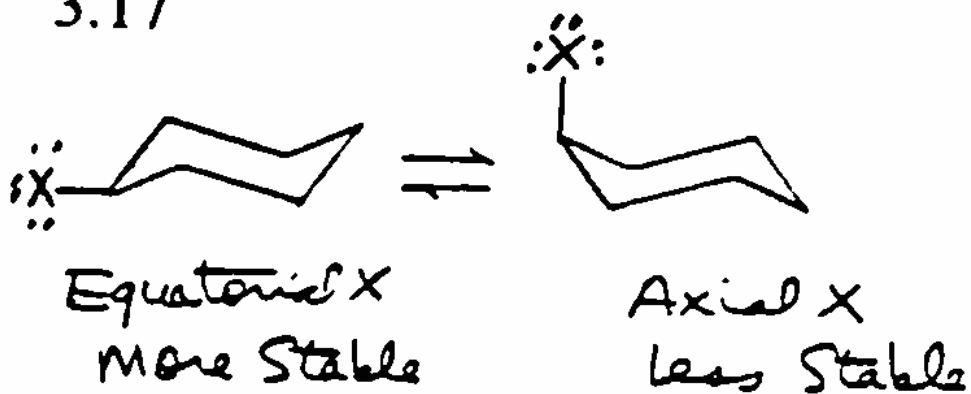
Larger

The much greater equatorial preference for CH_3 compared to the halogens reflects the relatively short length of the C-CH_3 bond (Table 3.4), and the fact that the C has three attached H atoms. The larger size for CH_3 compared to the halogens is also visible in the bond angle data for $(CH_3)_3$C-X in Table 3.5 since CH_3-C-CH_3 angles in $(CH_3)_3$C-X are always greater than CH_3-C-X angles.

*Boiling Points*. The boiling points of *fluoroalkanes*, and *chloroalkanes* show the same increase with increasing molecular mass as unbranched alkanes (Figure [graphic 3.19]). [graphic 3.19]   The boiling points for *bromoalkanes* and *iodoalkanes* also increase with molecular mass, but they are lower than we would predict from their absolute mass values. Nevertheless, when we add CH_2 groups to any of the haloalkanes, their boiling points increase by 25-30 °C per CH_2 group as is the case for alkanes (Chapter 1).

C-X Bond Strengths. The **strength** of C-X bonds decreases in the order C-F > C-Cl > C-Br >C-I that is opposite to the order of C-X *bond lengths*. Bond *strengths* are more properly called **bond energies** or **bond dissociation energies** (**D**). We compare values of *D* for C-X bonds in CH_3-X in Table 3.7.

Table 3.7. Approximate Bond Dissociation Energies for C-X Bonds in CH3-X

C-X Bond	D value (kJ/mol)
C-F	450
C-H	435
C-CH_3	370
C-Cl	350
C-Br	295
C-I	235

D is the amount of energy that we need to break a C-X bond (shown here as C**:**X to emphasize that the bond is a pair of electrons).

$$H_3C\text{:}X \quad + \quad \mathbf{D} \quad \rightarrow \quad H_3C\text{·} \quad + \quad \text{·}X$$
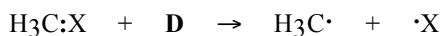
We will see in a later chapter that these D values reflect the relative stabilities of the halogen atoms (X·). We will also see that **chemical reactivity** of haloalkanes (R-X), in reactions where C-X bonds break, is greatest for those with the lowest D values. We also compare D values for C-X bonds to those of C-H and C-C bonds in Table 3.7.

3.3 Alcohols (R-OH)

You can think of **alcohols** (R-OH) as (1) organic derivatives of water (<u>H</u>-OH) where one of its <u>H</u>'s is replaced by an R group, or (2) as an alkane (R-<u>H</u>) where it's <u>H</u> is replaced by an OH group. [graphic 3.20]   Both of these views reflect the properties of alcohols since alcohols blend the characteristics of *water* and of *alkanes*.

Nomenclature (3.3A)

Alcohol nomenclature is fundamentally different from *haloalkane* nomenclature.

Systematic Names. We name *alcohols* as **alkanols** where the ending *ol* indicates the presence of OH on the carbon skeleton. For example, the replacement of an H on *methane* (CH_4) by OH gives **methanol** (CH_3OH), while replacement of an H on *ethane* (CH_3CH_3) by OH gives **ethanol** (CH_3CH_2OH). These names come from those of the corresponding *alkan<u>e</u>* by replacing <u>e</u> with *ol*.

When we substitute one OH for any one of the H's on CH_4 or any one of the H's on CH_3CH_3, we obtain just the single compounds named *methanol* and *ethanol* structures that we show above. This is not the case when we substitute an OH for an H on most other alkanes. For example substitution of OH for an H on *propane* gives two different *isomeric* alcohol. [graphic 3.21]
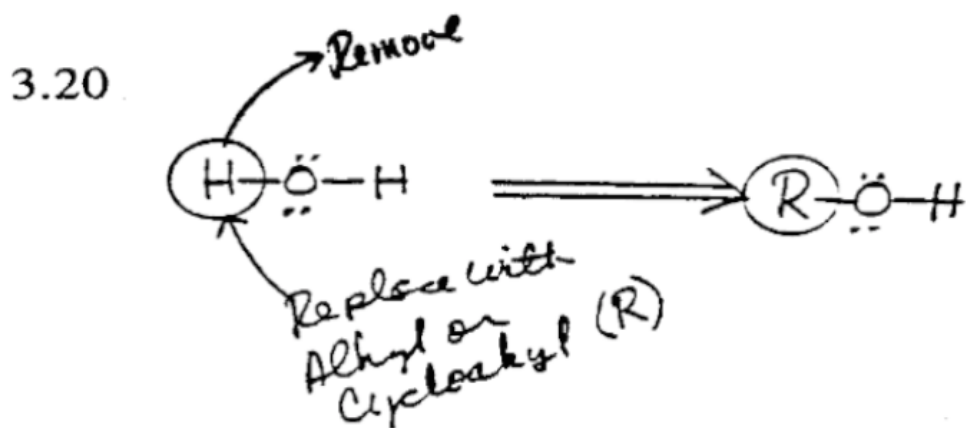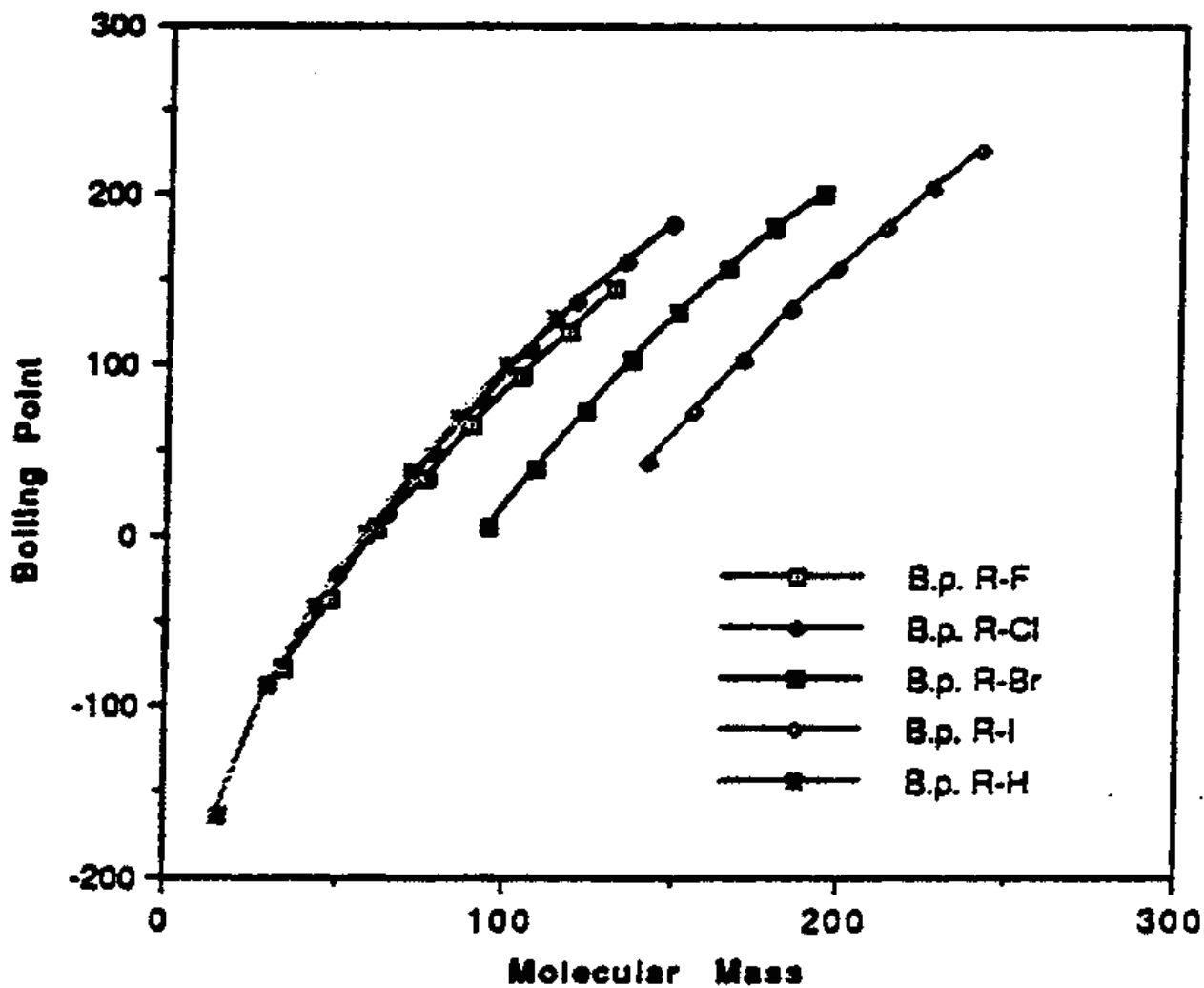
The names of these *isomers* are *1-propanol* and *2-propanol* where the numbers indicate the position of the OH group on the parent alkane chain. We name all alcohols, including those with other substituents (such as alkyl groups and halogen atoms) using the following three rules:

Rule 1. We choose the longest alkane chain with the attached OH group as the parent alkanol.

Rule 2. We assign C1 to the end carbon of the parent alkanol so that the OH is on the lowest number C and place the number of the C-OH carbon in front of the name of the parent alkanol.

Rule 3. We list the substituents on the parent alkanol, along with the number of the C to which they are attached, in alphabetical order in front of the name of the parent alkanol. [graphic 3.22]
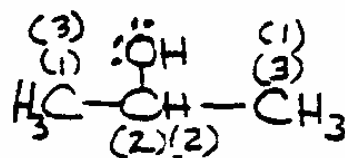
3.19   Boiling Points of R-X and R-H

3.20

3.21

$$H_3\overset{(3)}{C}-\overset{(2)}{C}H_2-\overset{(1)}{C}H_2-\overset{..}{\underset{..}{O}}H \qquad H_3\overset{(3)}{\underset{(1)}{C}}-\overset{:\overset{..}{O}H}{\underset{(2)(2)}{C}H}-\overset{(1)}{\underset{(3)}{C}}H_3$$
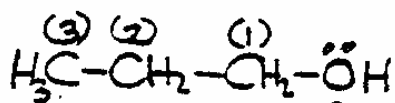
1-propanol   2-propanol

3.22

$$\overset{4}{C}H_3\overset{3}{C}H_2-\overset{2}{C}H-\overset{1}{C}H_2\overset{..}{\underset{..}{O}}H \qquad :\overset{..}{\underset{..}{B}}r-\overset{1}{C}H_2-\overset{:\overset{..}{O}H}{\underset{2}{C}H}-\overset{3}{C}H_3$$
$$\qquad\qquad CH_3 \qquad\qquad\qquad\qquad CH_3$$
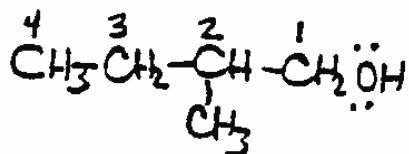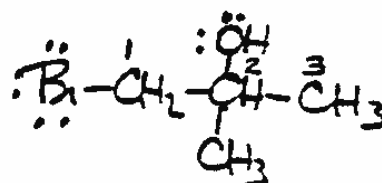
2-Methyl-1-butanol   1-bromo-2-methyl-2-
                            Propanol

1-ethyl-1-Cyclohexanol

Cyclopentanol

trans-2-methylcyclohexanol

Common Nomenclature. Organic chemists also refer to alcohols (R-OH) with simple R groups as "alkyl alcohols". Examples are *methyl alcohol*, *ethy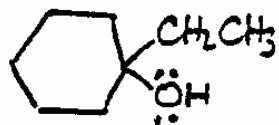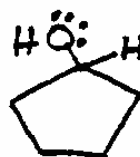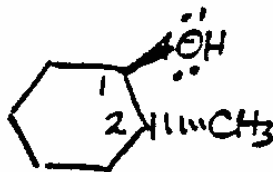l alcohol*, *isopropyl alcohol*, and *t-butyl alcohol*. [graphic 3.23]   This *common nomenclature* is analogous to common "alkyl halide" names such as *methyl chloride* for CH_3Cl.

> ***The OH Group as a Substituent***. We will see later that it is sometimes necessary to name and number the OH group as a substituent called the *"hydroxy"* group. Some ompounds, where another functional group takes precedence over the OH group in defining the root name of the compound, require this "substituent" nomenclature method. Examples are presented later in the text.
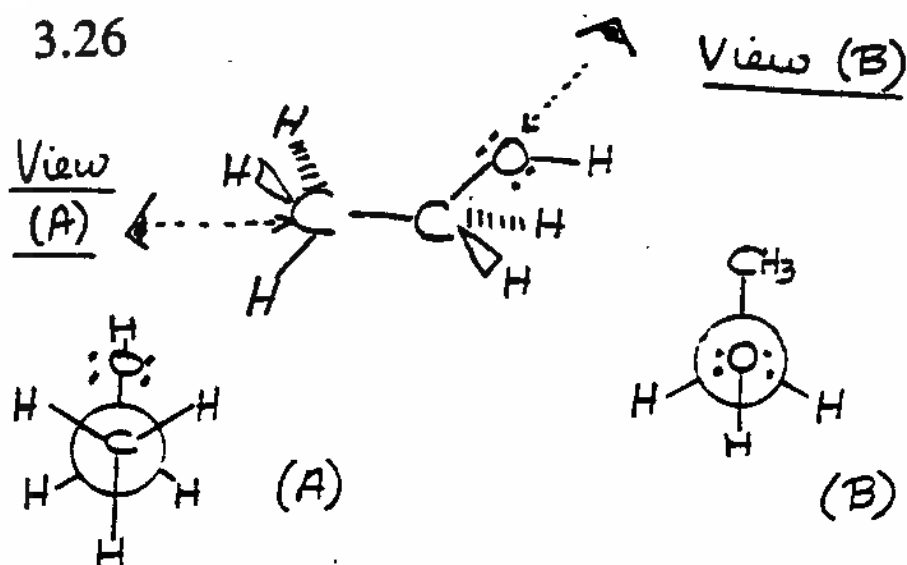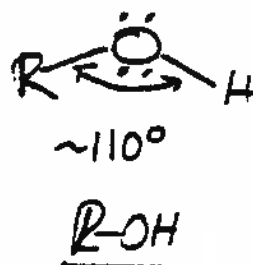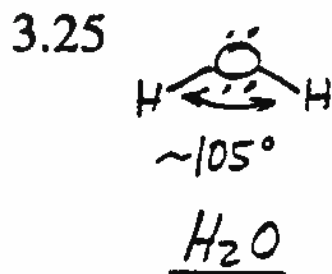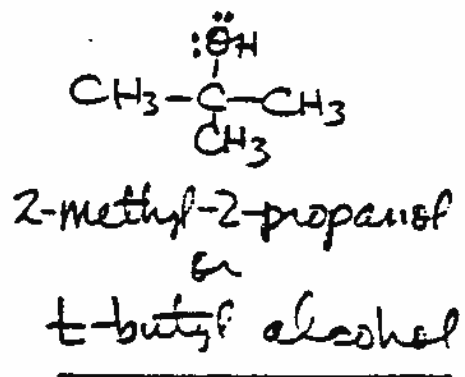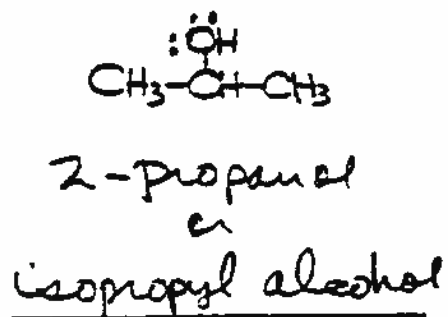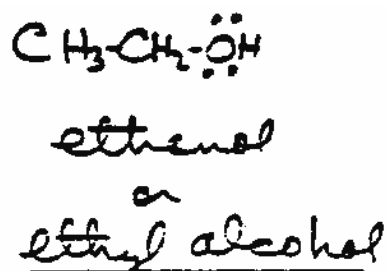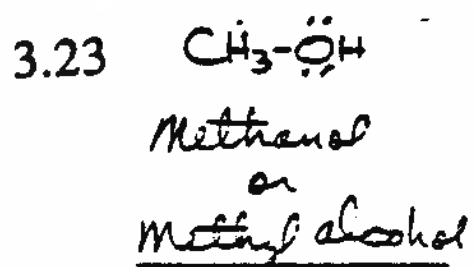
Properties of Alcohols (3.3B)

The properties of alcohols are strongly influenced by their OH group. The OH group causes low molecular mass alcohols to have properties more similar to those of *water* than those of *alkanes* or *haloalkanes* with the same number of C's.

Structure. Alcohols have R-O-H bond angles of 109° to 110° so we assign sp^3 hybridization to the O as we described in Chapter 1. These R-O-H angles are larger than the H-O-H bond angle of 105° because R groups are larger than H. [graphic 3.25]   The OH group can have various orientations with respect to the rest of the molecule due to rotation about the R-O bond. Calculations show that the most stable conformation of ethanol (CH_3CH_2OH) is that in Figure [graphic 3.26] . All groups are fully staggered along the C-C bond (Newman projection "A"), the O-C bond (Newman projection "B"), and the O-H hydrogen is *anti* to CH_3. [graphic 3.26]

> **Calculated Molecular Conformations**. The ethanol conformation in Figure [graphic 3.26] arises from calculations using computer software (Spartan 3.1, Wavefunction, Inc.) that determines molecular structures of organic molecules using "electronic structure theory". The most stable structure shown in Figure [graphic 3.26] is that of an isolated molecule of ethanol, however the most stable conformation in solution may not be exactly the same because of interactions between neighboring ethanol molecules described below.

Polarity. While alkanes and haloalkanes are very insoluble in water, low molecular mass alcohols are very water soluble and they also dissolve certain inorganic salts. These "water-like" properties of alcohols diminish as the number of C's in R increases (Table 3.8) because the properties of the of the non-polar R group overwhelm those of the polar OH group. [Table 3.8][next page]

3.23 $CH_3-\ddot{O}H$ $CH_3-CH_2-\ddot{O}H$

Methanol   ethanol
or   or
Methyl alcohol   ethyl alcohol

$CH_3-\underset{\overset{|}{:\ddot{O}H}}{CH}-CH_3$ $CH_3-\underset{\overset{|}{CH_3}}{\overset{\overset{:\ddot{O}H}{|}}{C}}-CH_3$

2-propanol   2-methyl-2-propanol
or   or
isopropyl alcohol   t-butyl alcohol

3.25

H_2O ~105°

$R-OH$ ~110°

3.26

View (B)

View (A)

(A)

(B)

Table 3.8. Solubility of Alcohols in Water (20°)

Alcohol	Solubility in H_2O (g/100 g)
methanol	∞
ethanol	∞
1-propanol	∞
1-butanol	8
1-pentanol	3
1-hexanol	1
1-heptanol	<1

These properties arise from the polar C-O and O-H bonds, but bond polarity by itself does not explain why properties of alcohols are so different from those of haloalkanes that also have polar bonds. [graphic 3.27]

Hydrogen Bonding (3.3C)

The polar OH group imparts special properties to alcohols.

   The OH Group Forms Hydrogen Bonds. Because the (δ+) H of the OH group has no electrons other than the electron pair in the O-H bond, it interacts with sites of high electron density such as unshared electron pairs on O atoms of neighboring alcohol molecules. [graphic 3.28]   The H on each O-H forms a weak **hydrogen bond** with an unshared electron pair on a partially negative O of a neighboring alcohol molecule creating a network of weak *hydrogen bonds* between alcohol molecules.   *Hydrogen bonding* in alcohols is analogous to that in liquid water where the network of hydrogen bonds is even more extensive because the O of HOH has two attached H's. [graphic 3.29]

   Effect on Boiling Points. We can see that *hydrogen bonding* significantly affects boiling points of alcohols by examining the boiling points of *propane*, *fluoroethane*, and *ethanol* (Table 3.9) whose molecular masses are similar.

Table 3.9. Boiling Points of an R-H, R-F, and R-OH with Similar Masses

Compound	Name	Molecular Mass	B.P. (°C)
$CH_3\text{-}CH_2\text{-}CH_3$	propane	44	-42
$CH_3\text{-}CH_2\text{-}F$	fluoroethane	48	-38
$CH_3\text{-}CH_2\text{-}O\text{-}H$	ethanol	46	+79

Ethanol is a *liquid*, with a boiling point more than 100° higher than those of the *gases* propane and fluoroethane, because its hydrogen bonds must break for it to boil. While strengths of hydrogen bonds (2 to 25 kJ/mol) are small compared to those of normal chemical bonds (250 to 450 kJ/mol) (Table 3.7), they have a big influence on the properties of alcohols

3.27

3.28

3.29
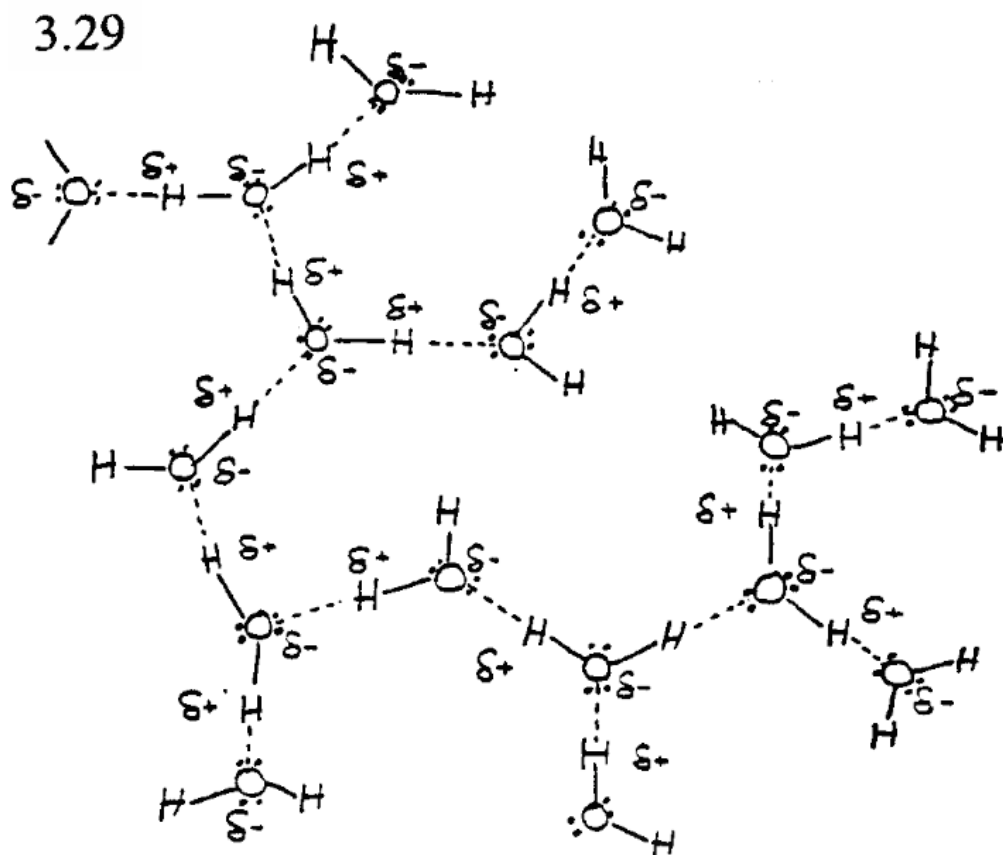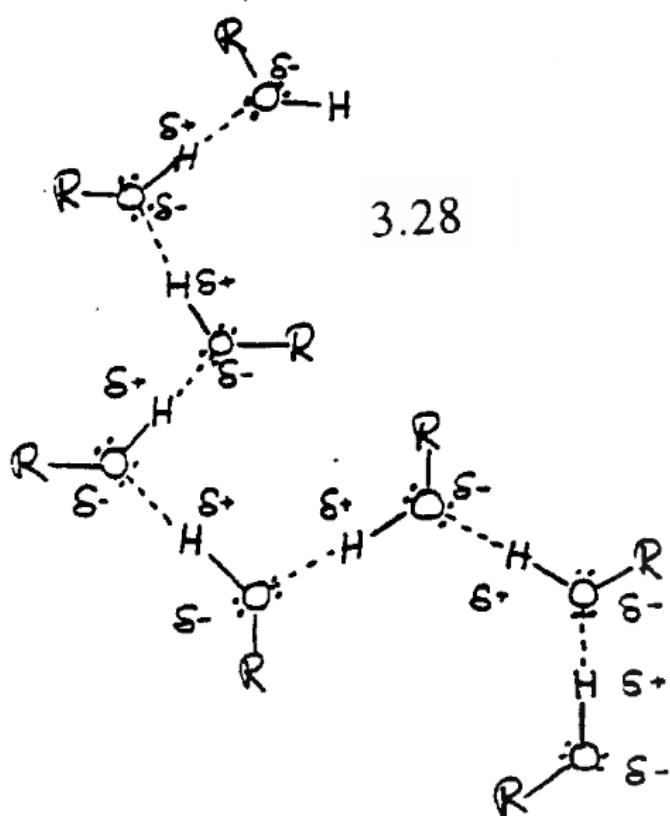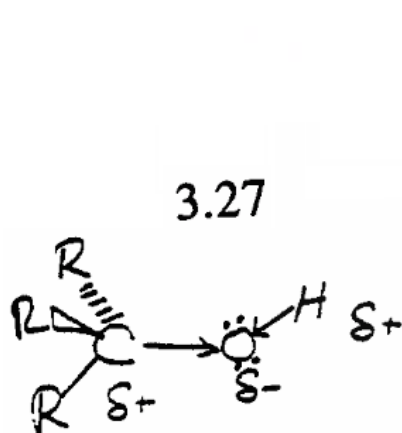
because hydrogen bonding is so extensive. In spite of the presence of hydrogen bonding, an increase in molecular mass of alcohols (Table 3.10) leads to an increase in boiling point (20° per CH_2 group) similar to that we saw for haloalkanes and alkanes (25-30° per CH_2).

Table 3.10. Boiling Points of Several Alcohols of Increasing Molecular Mass

Alcohol	b.p. (°C)	Δ b.p.
methanol	65	
ethanol	79	+14
1-propanol	97	+18
1-butanol	117	+20
1-pentanol	137	+20
1-hexanol	158	+21
1-heptanol	176	+18

Effect on Solubility. Hydrogen bonding allows salts like sodium chloride (NaCl) or potassium iodide (KI) to be partially soluble in alcohols because their Cl⁻ or I⁻ anions (generally represented as Z⁻) hydrogen bond to alcohol OH groups. [graphic 3.30]   The cations of these salts (Na^+ or K^+) (generally represented M^+) are stabilized in alcohol solutions not by hydrogen bonding, but by dipolar interactions with the partially negative O atoms. [graphic 3.31]   The mutual solubility of alcohols and water (see Table 3.8) results from hydrogen bonding since they can replace each other in their respective hydrogen bonding networks.

Hydrogen Bonding and Life. Without hydrogen bonding, H_2O should be a gas. The structurally similar compound H_2S is a gas (b.p. -61°) even though it has a higher molecular mass than H_2O because S-H bonds are relatively nonpolar (electronegativity of S is 2.7) and do not form effective hydrogen bonds.

Water is the medium in which life developed and is the most abundant molecule in living systems so it is likely that life would not exist if H_2O was not a liquid. Later in this text you will see that hydrogen bonding is also of crucial importance in determining three dimensional structures of biologically important molecules such as proteins and nucleic acids.
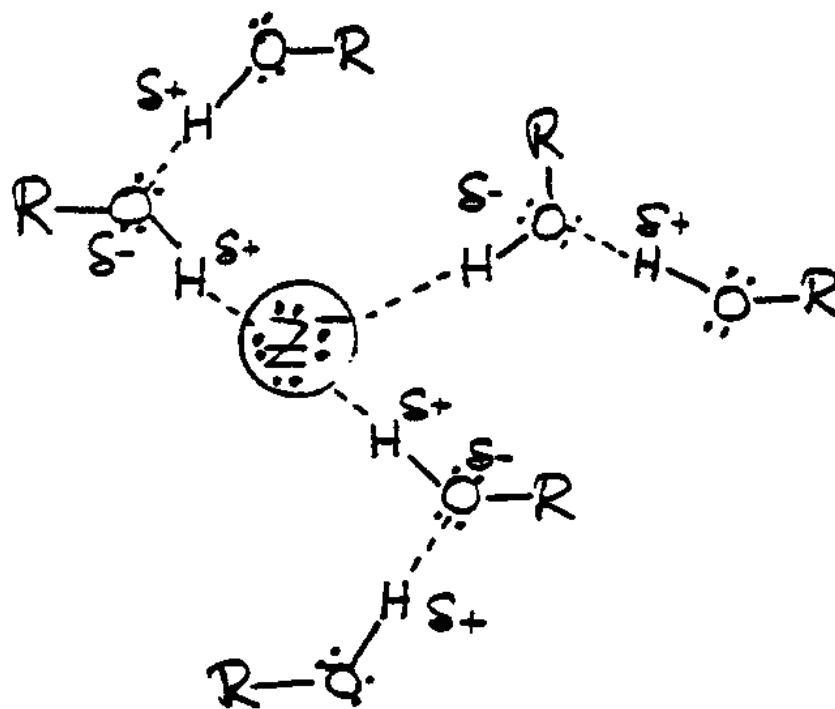
3.4 Ethers (R-O-R)

If we substitute an R group for the <u>H</u> on the O-<u>H</u> group of an alcohol (R-O-<u>H</u>), the resulting compounds R-O-R constitute a new class of organic compounds called **ethers**.
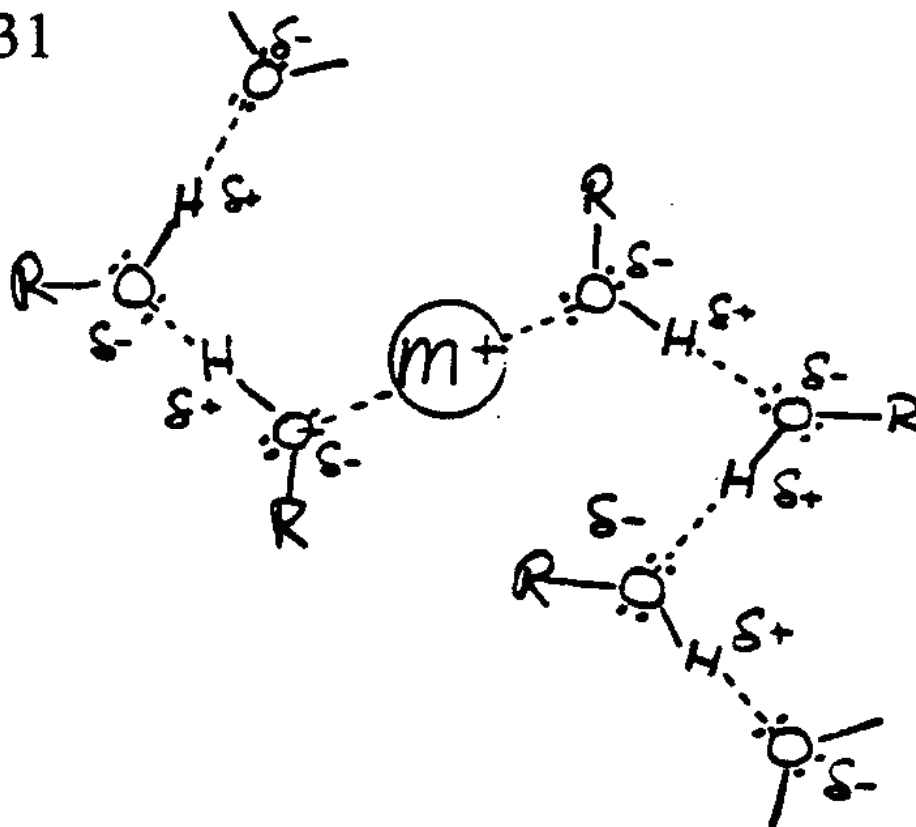
Physical Properties and Structure (3.4A)

The physical properties of *ethers* are dramatically different from those of *alcohols*.

3.30

3.31

Boiling Points. While the alcohol CH_3-OH is a liquid (b.p. +65°), the ether CH_3-O-CH_3 is a gas (b.p. -25°) even though it has a greater molecular mass. In contrast with alcohols, ethers are relatively insoluble in water and are poorer solvents for polar and ionic compounds. All of these differences are due to the absence of the O-H group in ethers that precludes formation of hydrogen bonds.

Bond Angles. R-O-R bond angles are larger than R-O-H bond angles because R groups are larger than H. [graphic 3.32]   While the R-O-R bond angle is significantly larger than 109.5°, we still consider O to be tetrahedral and sp^3 hybridized.

Nomenclature (3.4B)

We systematically name *ethers* using the nomenclature rules for *haloalkanes*.

Systematic Nomenclature. Choose one of the two R groups in ROR as the *parent alkane* (R-H) based on its greater size or complexity, and designate the remaining RO group as a *substituent* on that parent alkane. [graphic 3.33]   The RO substituents are **alkoxy groups** and two simple examples are **methoxy** (CH_3O) and **ethoxy** (CH_3CH_2O).

Common Nomenclature. Organic chemists also refer to simple ethers by *common names*. You can form these by alphabetically listing the alkyl group names of each of the two R's before the word *ether*. [graphic 3.34]
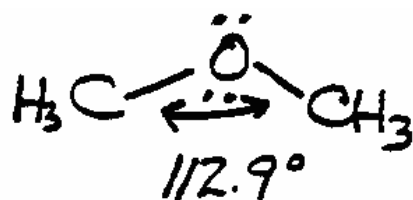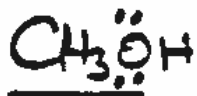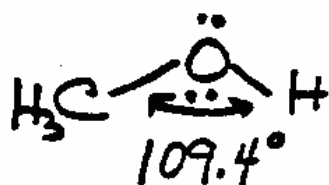
Cyclic Ethers (3.4C)

Since the O atom of ethers is bonded to two C's, that O can be included in a ring of C atoms. [graphic 3.35]   We will sometimes refer to *cyclic ethers* as **heterocyclic** compounds (or **heterocycles**) because their rings contain one or more atoms other than C.

Nomenclature. Using systematic nomenclature, we name cyclic ethers as **oxacycloalkanes** where the prefix *oxa* indicates that an O has replaced a CH_2 in a cycloalkane ring. [graphic 3.36]   However, certain cyclic ethers are always referred to by nonsystematic names also shown in this figure. Organic chemists call three-membered ring ethers (*oxacyclopropanes*) **epoxides**. The simplest *epoxide* has the common name **ethylene oxide**. Epoxides have significant ring strain so we will see in later chapters that they undergo reactions that do not occur with most other cyclic or noncyclic ethers.

Properties. Ethers are poorer solvents for polar and ionic compounds than alcohols because they cannot form hydrogen bonds. However they are better solvents for these

3.32

$H_3C \xrightarrow{\longleftrightarrow} H$
$109.4°$

$CH_3\ddot{\underline{O}}H$

$H_3C \xrightarrow{\longleftrightarrow} CH_3$
$112.9°$

$CH_3-\ddot{\underline{O}}-CH_3$

3.33

$CH_3CH-\overset{:\ddot{O}CH_3}{CH}CH_2CH_3$
$\underset{CH_3}{|}$
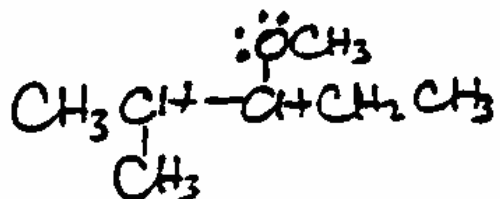
3-methoxy-2-Methylpentane
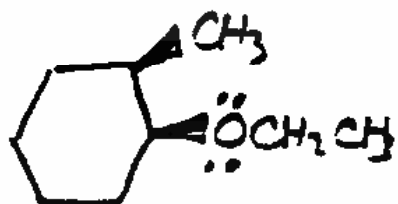
cis - 1-ethoxy-2-Methyl-Cyclohexane

3.34

$CH_3CH_2-\ddot{\underline{O}}-CH_2CH_3$
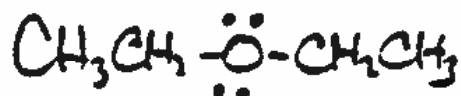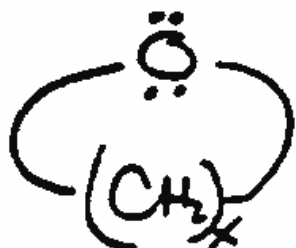
ethoxyethane

or

diethyl ether

Methoxycyclohexane

or

Cyclohexyl Methyl ether

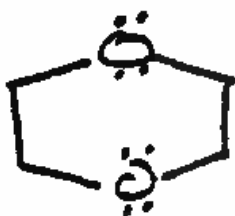3.35

Ö

(CH₂)ₓ

Cyclic Ether

"Oxacycloalkane"

3.36

Oxacyclopropane
or
ethylene oxide

Oxacyclopentane
or
tetrahydrofuran

1,4-dioxacyclohexane
or
dioxane

compounds than *alkanes*, so organic chemists often use **tetrahydrohydrofuran** (**THF**) (*oxacyclopentane*) or **dioxane** (*1,4-dioxacyclohexane*), as solvents for polar reagents or reactants that undergo unwanted reactions with the OH groups of alcohols or water. *THF* and *dioxane* also dissolve a variety of salts that have metal cations such as Na^+ or K^+ because they solvate the metal cation (represented as M^+) through dipolar interactions in the same way that alcohols solvate metal cations. [graphic 3.37]   They are better solvents than *acyclic* ethers because the ring minimizes steric interactions between the carbons attached to O and the M^+ ion. [graphic 3.38]

> **Crown Ethers**. Organic chemists have created a vast array of cyclic ethers, referred to as **crown ethers,** that have multiple oxygen atoms in the same ring. [graphic 3.39]   Crown ethers are particularly effective at binding metal cations such as Li^+, Na^+, and K^+ because these cations fit into the center of the molecule where they interact by dipolar attraction with ring O's. [graphic 3.40]   As a result, ionic salts insoluble in organic solvents without OH groups often dissolve in crown ethers.
>
> Dr. Charles Pedersen, working at the E.I. duPont Company, discovered crown ethers in the 1960's. Professor Donald Cram of UCLA subsequently prepared many crown ethers and utilized them in a variety of chemical reactions. Professor Jean-Marie Lehn of Université de Strasbourg independently prepared and studied the properties of a variety of crown-ether-like molecules called *cryptands* that are similar to crown ethers. For these achievements, they shared the 1987 Nobel prize in chemistry.

3.5 Amines (RNH$_2$, R$_2$NH, R$_3$N)

The best way to picture *amines* is as organic derivatives of ammonia (NH_3) where alkyl or cycloalkyl R groups have replaced one, two, or three of the H's on NH_3 to give *RNH$_2$*, *R$_2$NH*, or *R$_3$N*.

1°, 2°, and 3° Amines (3.5A)

We call amines with one R (RNH$_2$) **primary (1°)** amines, those with two R's (R$_2$NH) **secondary (2°)** amines, and those with three R's (R$_3$N) **tertiary (3°)** amines. [graphic 3.41] The inclusion of *RNH$_2$*, *R$_2$NH*, and *R$_3$N* in a single class called *amines* is adramatic contrast to the different classes for *ROH* and *ROR* that we can comparably view as arising from H_2O by replacement of one or both H's with R groups. Organic chemists place *alcohols* (ROH) and *ethers* (ROR) in different classes because they have very different properties. In contrast, 1°, 2°, and 3° *amines* have very similar properties so they are all classified as *amines*. The most important of these common properties, that they also share with ammonia (NH_3), is their *basicity*. Like ammonia, all amines accept protons from both weak and strong acids as we will describe in the next major section of this chapter. [graphic 3.42]

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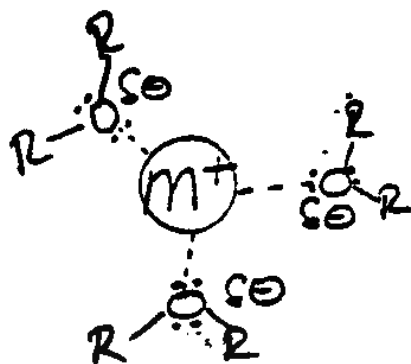
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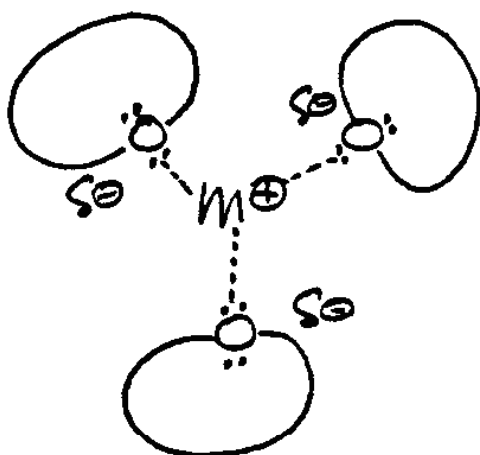
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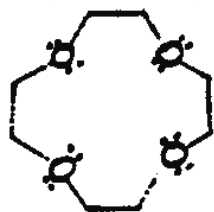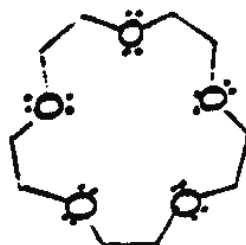
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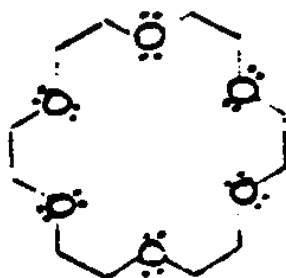
18-Crown-6

3.40

3.41

$$R-\ddot{N}\!\!<^H_H \qquad R-\ddot{N}\!\!<^R_H \qquad R-\ddot{N}\!\!<^R_R$$

or   or   or

$$R\ddot{N}H_2 \qquad\qquad R_2\ddot{N}H \qquad\qquad R_3\ddot{N}$$

Primary (1°) Secondary (2°) Tertiary (3°)

<u>Amine</u>   <u>Amine</u>   <u>Amine</u>

3.42 $\overset{\cdot\cdot}{N}H_3 \xrightarrow{\;Acid\,(H^+)\;} NH_4^+$

Ammonia

$$R_3N: \xrightarrow{\;Acid\,(H^+)\;} R_3\overset{+}{N}H$$
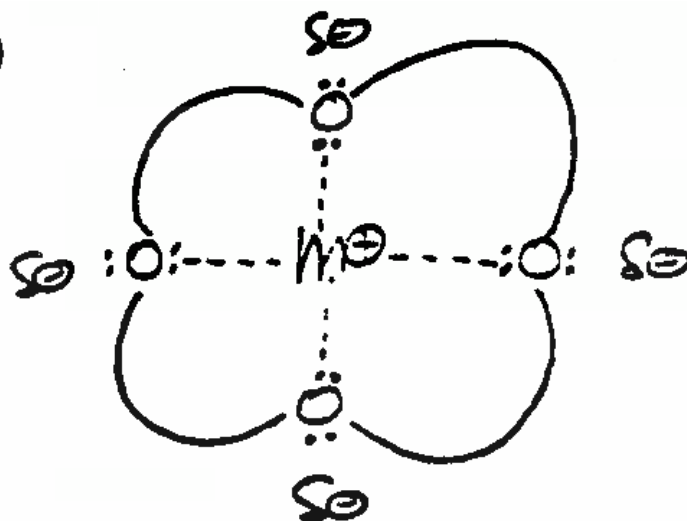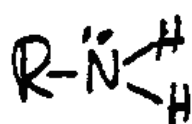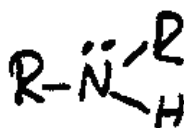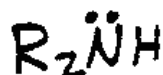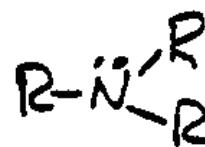
Amine

Nomenclature (3.5B)

Systematic nomenclature for *amines* is analogous to that of *alcohols*. [graphic 3.43]

1° Amines (RNH$_2$). For *primary* (*1°*) amines *R-NH$_2$*, the ending *"amine"* replaces the ending "*e*" in the name of the parent alkane that has the substituent NH$_2$ according to the following two rules:

Rule 1. Choose the longest alkane chain with the NH$_2$ as the parent "alkanamine."

Rule 2. Number the parent "alkanamine" so that the C with the NH$_2$ group has the lowest possible number and place that number in front of the name "alkanamine".

We then list substituents on the <u>carbon skeleton</u> of the parent *alkanamine*, in alphabetical order, in front of the *alkanamine* name along with the numbers of their attached carbons.

2° and 3° Amines (R$_2$NH and R$_3$N). We name *2°* and *3°* amines as "N-substituted 1° alkanamines" using the following rules:

Rule 1. Select the R group on N with the longest alkane chain as the parent 1° alkanamine and name it as described above for 1° amines.

Rule 2. Name other R groups on N as alkyl substituents on the parent 1° alkanamine and list them in alphabetical order at the beginning of the parent 1° alkanamine name preceded by the letter "N".

These examples show the application of these rules to several different amines. [graphic 3.44]   The names in parentheses are *common* names described below.

Common Nomenclature. You can name simple amines as **alkylamines** in the same way that you named simple alcohols or simple haloalkanes as *alkyl alcohols* or *alkyl halides*. [graphic 3.44a]   Designate each R group on N as an "alkyl" group and place it in alphabetical order before the word "amine" (see Figure [graphic 3.44]). Unlike *alkyl halide* and *alkyl alcohol* common names, there is no space between the *alkyl* names and the *amine* ending. Organic chemists routinely prefer to use the common names of simple amines rather than their systematic names.

3.43

Some Amines and Their Names

$CH_3-\ddot{N}H_2$

methanamine

$CH_3CH_2-\ddot{N}H_2$

ethanamine

$CH_3-CH_2-CH_2-\ddot{N}H_2$

1-propanamine

$CH_3-\overset{:\ddot{N}H_2}{CH}-CH_3$

2-propanamine

$CH_3-CH_2-\overset{\underset{CH_3}{|}}{CH}-CH_2\ddot{N}H_2$
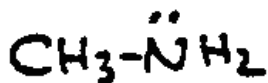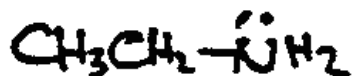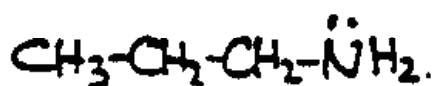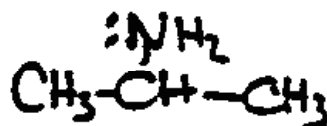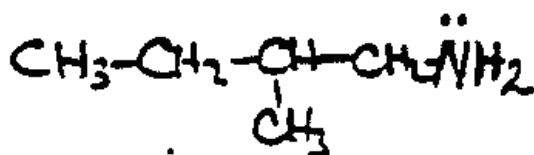
2-methyl-1-butanamine

1-methylcyclohexan-amine

3.44   1° Amines

CH₃CH₂CH₂–ṄH₂   1-Propanamine
                      (propyl amine)

CH₃–CH–CHCH₃   2-butanamine
      :NH₂

2° Amines

CH₃–Ṅ⟨CH₃/H   N-Methyl methanamine
                      (dimethylamine)

CH₃CH₂–Ṅ⟨CH₃/H   N-methyl ethanamine
                      (ethylmethylamine)

3° Amines

  N,N-dimethylcyclohexanamine
                      (cyclohexyldimethylamine)

CH₃CH₂CH₂–Ṅ⟨CH₂CH₃/CH₃   N-ethyl-N-methyl-1-propanamine
                      (ethylmethylpropylamine)

3.44a

$CH_3-CH_2-\overset{..}{N}H_2$

Ethanamine

or

ethylamine

$:NH_2$
$CH_3-CH-CH_3$

2-propanamine

or

isopropylamine

$CH_3-\overset{:NH_2}{\underset{CH_3}{\overset{|}{C}}}-CH_3$

2-methylpropanamine

or

t-butylamine

Cyclohexanamine

or

Cyclohexylamine

3.45

azacyclopentane

or

Pyrrolidine

azacyclohexane

or

Piperidine

CH_3
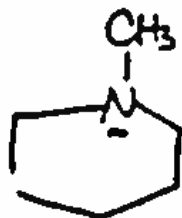
N-Methylazacyclohexane

or

N-Methylpiperidine

   Amino Substituents. We name the NH$_2$ group as an "*amino*" group if other functional groups are present and take precedence in determining the root name of the molecule. For example, the systematic name of HOCH$_2$CH$_2$CH$_2$NH$_2$ is 3-amino-1-propanol since OH takes precedence over NH$_2$ (see Appendix xx). RNH or R$_2$N groups are "N-alkylamino" or "N,N-dialkylamino" groups, respectively.

   Cyclic Amines. Cyclic amines have N as part of a ring structure and are named **azacycloalkanes**. [graphic 3.45]   The prefix *aza* indicates that a ring CH$_2$ group of a cycloalkane has been replaced by N-H. Cyclic amines with N-R groups instead of N-H groups are **N-alkylazacycloalkanes**. The common names of certain *azacycloalkanes* (Figure [graphic 3.45]) are more popular than their systematic names. Cyclic amines along with cyclic ethers are *heteocyclic* compounds.

Structure and Properties of Amines *(3.5C)*
Structures and properties of amines are similar to those of ammonia (NH$_3$).

   Structure. Both ammonia and amines have **pyramidal** structures. [graphic 3.46] [graphic 3.47]   Although bond angles at N usually differ somewhat from 109.5°, we conseder N to be sp^3 hybridized with its unshared electron pair in an sp^3 atomic orbital as we described in Chapter 1. The bond angles at N increase as we replace H's on N with R groups because R's are larger than H.

The **pyramidal** amino group can have several orientations with respect to the rest of the molecule due to rotation about C-N bonds. The most stable conformation of ethanamine (CH$_3$CH$_2$NH$_2$) has groups completely staggered along the C-C bond (Newman projection "A"), and N-C bond (Newman projection "B"), while the N-H bonds are *gauche* to the CH$_3$. [graphic 3.48]   The unshared electron pair is *anti* to CH$_3$ because unshared electron pairs in atomic orbitals generally behave as if they are larger than electron pairs in C-H bonds.

   Inversion at Nitrogen. Amines (and ammonia) undergo rapid reversible **inversion** from one pyramidal form to another by way of a higher energy planar form. [graphic 3.49]   While the N is hybridized sp^3 in the *pryamidal* forms, it is hybridized sp^2 in the *high energy planar* form.

   Polarity and Hydrogen Bonding. C-N and N-H bonds are polar with partially negative (δ-) N and partially positive (δ+) C (or H) because N is more electronegative than C (or H). [graphic 3.50]   Because of this polarity, N-H bonds of *1° and 2° amines* can participate in

3.46

NH_3 $R-NH_2$

3.47

$CH_3\ddot{N}H_2$ $(CH_3)_2\ddot{N}H$ $(CH_3)_3\ddot{N}$

3.48

View (B)

View
(A)

:NH₂

(A)

CH₃

(B)

3.49

Unstable
Planar
Form
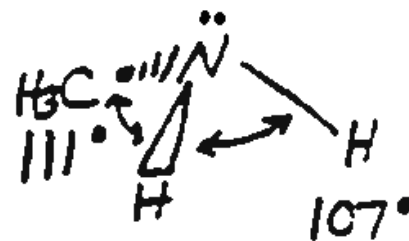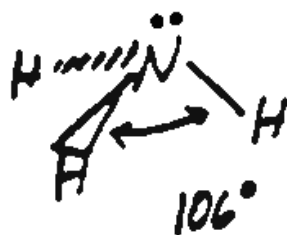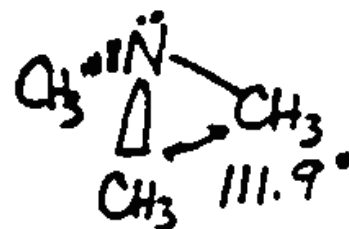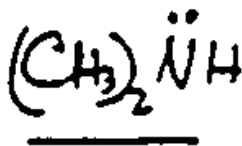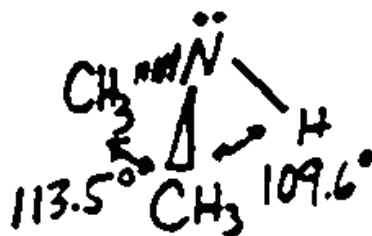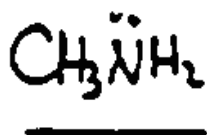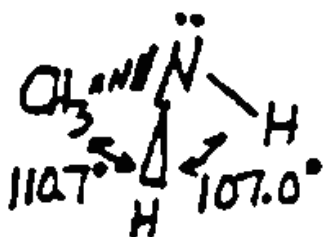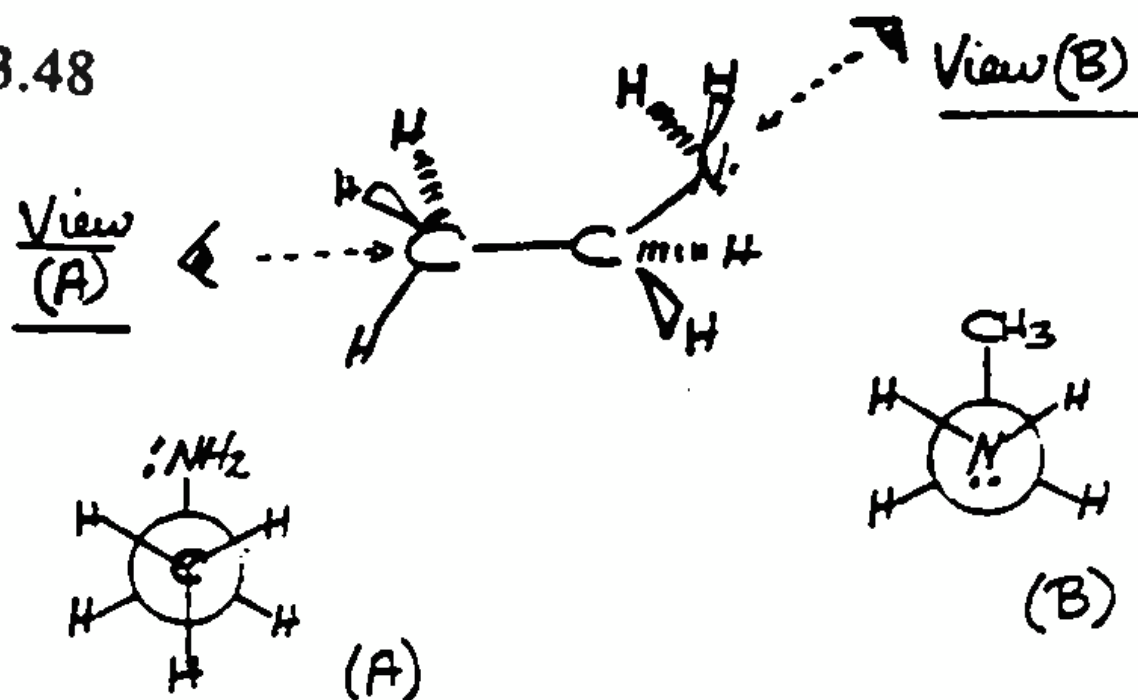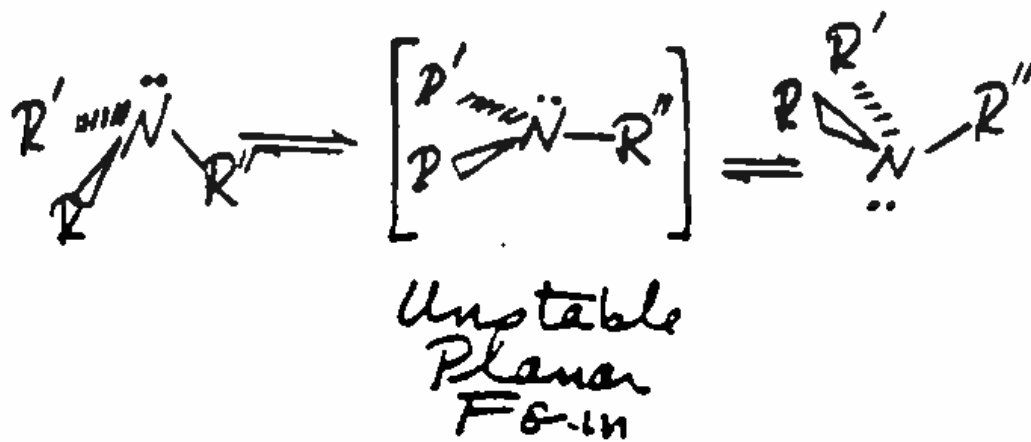
3.50
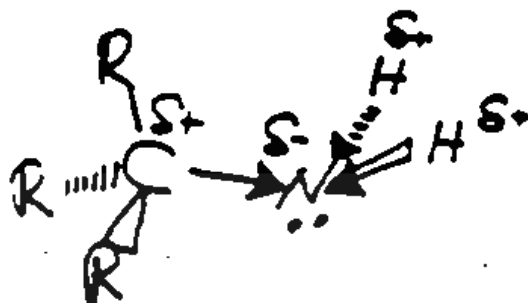
hydrogen bonding like O-H bonds of water (HOH) and alcohols (ROH). However, the electronegativity of N (2.9) is less than that of O (3.4), so N-H bonds are less polar than O-H bonds, and their hydrogen bonds are correspondingly weaker than O-H hydrogen bonds. This weak N-H hydrogen bonding leads to boiling points for *1° and 2° amines* that are significantly higher than those of *alkanes* of comparable molecular mass, but significantly lower than those of comparable *alcohols* as you can see in Table 3.11.

Table 3.11. Comparative Boiling Points of Alkanes, Amines, and Alcohols

Compound	Mass	Boiling Point (°C)
CH_3-CH_3	30	-89
CH_3-NH_2	**31**	**-6**
CH_3-OH	32	+65
CH_3-CH_2-CH_3	44	-42
CH_3-CH_2-NH_2	**45**	**+17**
CH_3-CH_2-OH	46	+79

While 2° amines also form hydrogen bonds, 3° amines do not since they have no N-H bonds. [graphic 3.51]   As a result, you can see in Table 3.12 that boiling points of 3° amines are closer to those of alkanes of comparable molecular mass and structure than is the case for 1° or 2° amines. CH_3NH_2 (two N-H bonds) boils 83° higher than CH_3CH_3 (ethane), and $(CH_3)_2NH$ (one N-H bond) boils 49° higher than $(CH_3)_2CH_2$ (propane), but the boiling point of $(CH_3)_3N$ (no N-H bonds) is only 16° higher than that of $(CH_3)_3CH$ (2-methyl-propane) with almost the same molecular mass. The small difference between boiling points of $(CH_3)_3N$ and $(CH_3)_3CH$ reflects the greater polarity of the amine.

Table 3.12. Boiling Points of Some 1°, 2°, and 3° Amines and Comparable Alkanes

	Amine/Alkane	b.p. (°C)	Δ b.p. (°C)
(1°)	CH_3NH_2	-6	+83
	CH_3CH_3	-89	
(2°)	$(CH_3)_2NH$	+7	+49
	$(CH_3)_2CH_2$	42	
(3°)	$(CH_3)_3N$	+4	+16
	$(CH_3)_3CH$	-12	

Bond Strengths and Bond Lengths. C-N bonds in amines are similar in *strength* (*bond dissociation energy*, *D*) and *length* to C-O and C-C bonds, while their N-H bonds are similar to O-H and C-H bonds (Table 3.13)[next page].

3.51

2° Amines

H-Bonding

3° Amines

No H-Bonding

3.52

Ammonia

Ammonium Ion

3.53

1°, 2°, or 3° Amine

Alkanaminium Ion
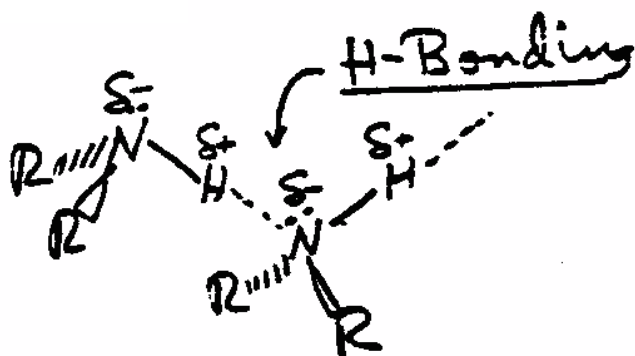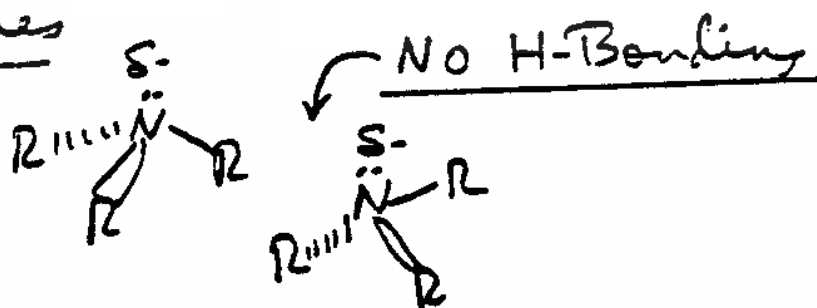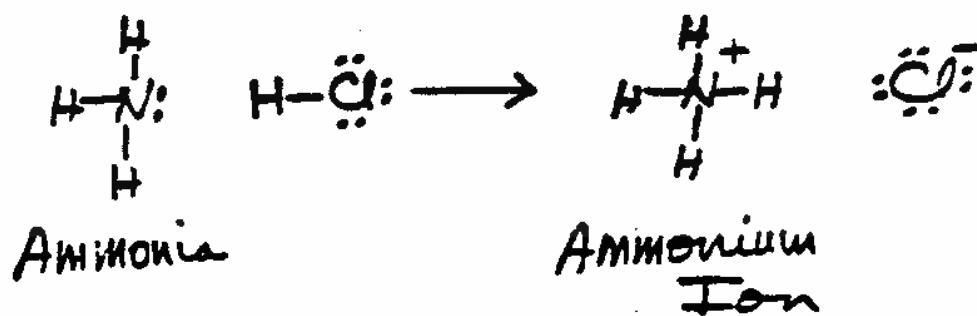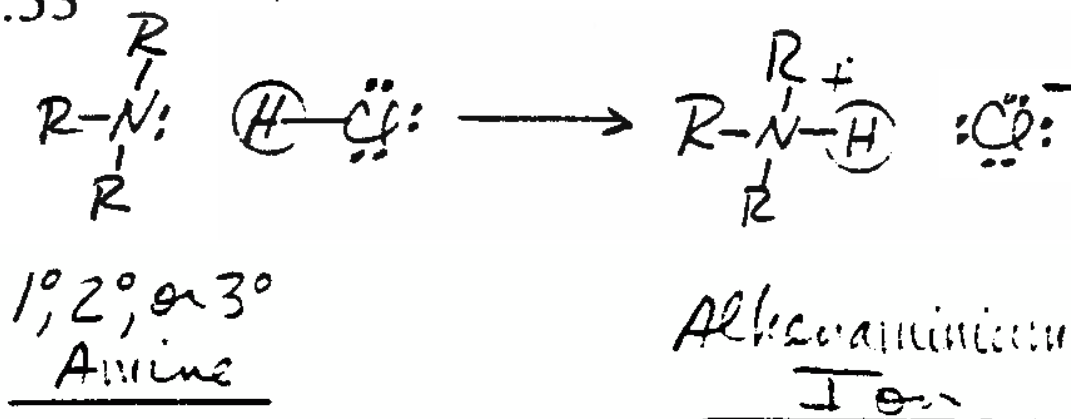
Table 3.13. Approximate Bond Strengths and Bond Lengths in
CH_3NH_2, CH_3OH, and CH_3CH_3.

Bond	D, (kJ/mol)	Bond Lengths, (Å)
C-N	330	1.45
C-O	380	1.40
C-C	370	1.53
N-H	430	1.00
O-H	430	0.94
C-H	435	1.11

3.6 Amines are Organic Bases

You learned in general chemistry that ammonia is a **base** because it accepts a proton from **acids** such as HCl to form the **ammonium** ion. [graphic 3.52]   Since 1°, 2°, and 3° amines undergo similar reactions with acids, we call them **organic bases**. [graphic 3.53]

Study Hints for this Section. We explore amine basicity, and review general concepts of basicity and acidity, in this section. It is important that you spend extra time with each part of this section before you proceed to the next part. Each part of this section expands on concepts that we present in the previous part. You may not fully understand a particular part even after a second careful reading. If that is the case, you might try reading the following part to see if it helps you. If you are still confused, it is important to speak with your instructor about your concerns. Some preliminary help early in your reading will probably have a tremendous positive benefit on your ability to understand this material on amine basicity.

Why is Basicity (and Acidity) Important? Since you spent a significant amount of time studying acidity and basicity in your general chemistry course, you may wonder why it is a topic of this chapter. One reason is that amines are bases, so it is appropriate to review concepts of basicity and acidity here. It is even more important for you to understand the practical consequences of the basicity or acidity of organic compounds with respect to organic chemistry as well as other courses that you may subsequently take.

A particularly important consequence is that a basic functional group such as NH_2 can simultaneously exist in two different forms with very different properties (*e.g.*, $R-NH_2$ and $R-NH_3^+$), under conditions routinely encountered. For example we will see that each of these forms can be the dominant form in a water solution depending on the acidity or pH of that solution. This is not equally true for other functional groups like halogens (X) in haloalkanes, or the OH or OR functional groups in alcohols and ethers. No matter what the pH of the water solution, a haloalkane (RX) in water remains RX, and the same is largely true for ethers (ROR) and alcohols (R-OH).

Amine functional groups are present in proteins and other bioorganic compounds where they play an important role in determining the overall structures of these compounds. As a result, the easy interconversion under "normal" conditions between $R-NH_2$ and $R-NH_3^+$ has dramatic effects on the structures of these bioorganic molecules and thus on their biological activity.

You will use the concepts of acidity and basicity that we introduce in this chapter throughout this text and your organic chemistry course. It may surprise you to learn that acidity and basicity are also major topics of courses such as *biochemistry*, *molecular biology*, and *physiology*. For these reasons, it is important that you carefully study this material and do your best to understand these concepts.

Aminium Ions (3.6A)

The RNH_3^+, $R_2NH_2^+$, and R_3NH^+ ions formed in the reactions of acids with 1°, 2°, and 3° amines, are analogous to the tetrahedral ammonium ion (NH_4^+)(Figures [graphic 3.52] and [graphic 3.53]).

Nomenclature. The general *systematic* name of these ions is **alkanaminium**, but their general *common* name is **alkylammonium**. For example, reaction of an acid with *methanamine* (CH_3NH_2) gives the *methanaminium* ion ($CH_3NH_3^+$) that we commonly refer to as the *methylammonium* ion (Table 3.13a).

Table 3.13a. Systematic and Common Names of Aminium Ions.

Aminium Ion	Systematic Name	Common Name
$CH_3NH_3^+$	methanaminium	methylammonium
$(CH_3)_2NH_2^+$	N-methylmethanaminium	dimethylammonium
$(CH_3)_2NH(CH_2CH_3)^+$	N,N-dimethylethanaminium	ethyldimethylammonium

Protonation of Amines. In the reaction between an amine and an acid such as HCl, HCl transfers an H^+ (a proton) to the unshared electron pair on N (Figure [graphic 3.53]). The unshared electron pair on N becomes the new N-H bond in the aminium ion (RNH_3^+, $R_2NH_2^+$, or R_3NH^+) so that N has four bonds and no unshared electron pair. The pair of electrons in the H-Cl bond remains with Cl causing it to become a chloride ion (Cl^-) so the number of unshared electron pairs on Cl increases from three in H-Cl to four in Cl^-.

Electron Octets and Ionic Charges on N and Cl. The N in aminium ions and ammonium ion (NH_4^+), and the Cl of the chloride ion (Cl^-), have octets of electrons in their outer valence shells just as the N in amines or ammonia (NH_3), and the Cl in H-Cl. A chemical bond (2 electrons) replaces an unshared electron pair (2 electrons) or *vice-versa* during the reaction of ammonia or an amine with H-Cl

(Figures [graphic 3.52] and graphic [3.50]). The positive charge is present on NH_4^+ (and aminium ions) because N of NH_3 (or an amine) has gained a proton (+1) without gaining any additional electrons. The negative charge is present on Cl^- because Cl of H-Cl has lost a proton without losing any of its electrons.

Basicity of Amines (3.6B)

Strong acids such as HCl quantitatively (completely) transform amines into aminium ions. In contrast, *weak acids* such as water only protonate a fraction of the amine molecules in an aqueous solution. [graphic 3.54] The result of mixing an amine with water is an equilibrium mixture containing both the amine and aminium ion (*e.g.*, $R-NH_2$ and $R-NH_3^+$) analogous to the *equilibrium mixture* of NH_3 and NH_4^+ established when NH_3 dissolves in water. [graphic 3.55] We will focus the following discussion of amine basicity first on 1° amines ($R-NH_2$), however it applies equally to 2° and 3° amines.

Conjugate Acids and Bases. It is important to understand the nature of *chemical equilibrium* processes like that involving NH_3 and NH_4^+ (or RNH_2 and RNH_3^+) in water (Figures [graphic 3.54] and [graphic 3.55]). The *forward* and *reverse* arrows in the equilibrium equation mean that NH_3 and H_2O constantly undergo reaction with each other to form NH_4^+ and ^-OH, while NH_4^+ and ^-OH constantly undergo reactions to form NH_3 and H_2O. These reactions have very fast rates so the relative concentrations of the individual chemical species do not change once they are at equilibrium.

In the **forward** reaction, NH_3 acts as a base accepting a proton from H_2O to form NH_4^+. [graphic 3.56] In the **reverse** reaction, NH_4^+ acts as an acid donating a proton to a base to regenerate NH_3. Because NH_4^+ and NH_3 are in equilibrium, we call them a **conjugate acid-base pair**, and H_2O and ^-OH are also a *conjugate acid-base pair*. We can describe the equilibrium mixture of an *aminium ion* ($R-NH_3^+$) and an *amine* ($R-NH_2$) in water in the same way. Amines are *weak bases* and water is a *weak acid* so both the conjugate acid $R-NH_3^+$ and its base $R-NH_2$ are simultaneously present in the water solution.

More Details about these Equilibria. NH_4^+ (or RNH_3^+) and ^-OH can react with each other in water to give NH_3 (or RNH_2) and H_2O (reaction 1), but reactions 2 and 3 also lead to the overall conversion represented in reaction 1.

NH_4^+ (RNH_3^+) +	^-OH	$\rightarrow$	NH_3 (RNH_2)	+	H_2O	(1)
NH_4^+ (RNH_3^+) +	H_2O	$\rightarrow$	NH_3 (RNH_2)	+	H_3O^+	(2)
H_3O^+ +	^-OH	$\rightarrow$	H_2O	+	H_2O	(3)

3.54

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: \quad H-\overset{..}{\underset{..}{O}}-H \quad \rightleftharpoons \quad R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}}}-H \quad \quad \overset{-}{:}\overset{..}{\underset{..}{O}}H$$

3.55

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: \quad H\overset{..}{\underset{..}{O}}H \quad \rightleftharpoons \quad H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}}}-H \quad \quad \overset{-}{:}\overset{..}{\underset{..}{O}}-H$$

3.56

Forward Reaction

| base | acid | | Conjugate acid of :NH₃ | Conjugate base of H₂O |

$$\cdot NH_3 \quad H_2\overset{..}{\underset{..}{O}} \quad \rightleftharpoons \quad NH_4^{\oplus} \quad :\overset{..}{\underset{..}{O}}H$$

Reverse Reaction

Conjugate base of NH₄⊕   Conjugate acid of ⊖OH   acid   base
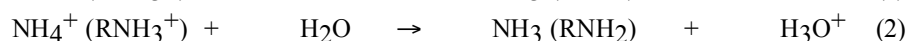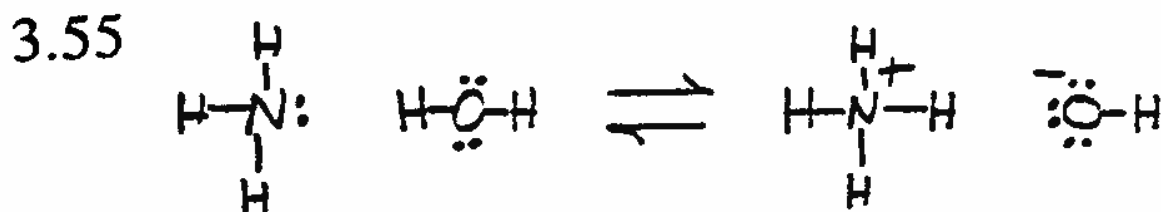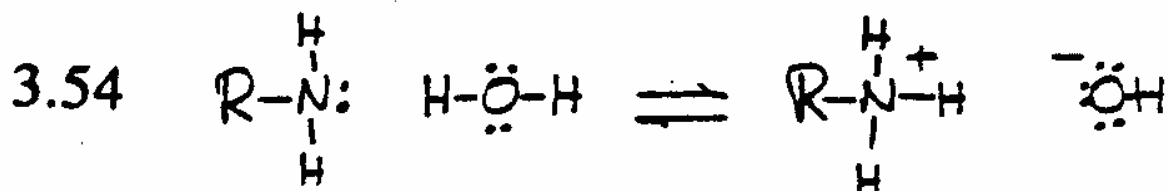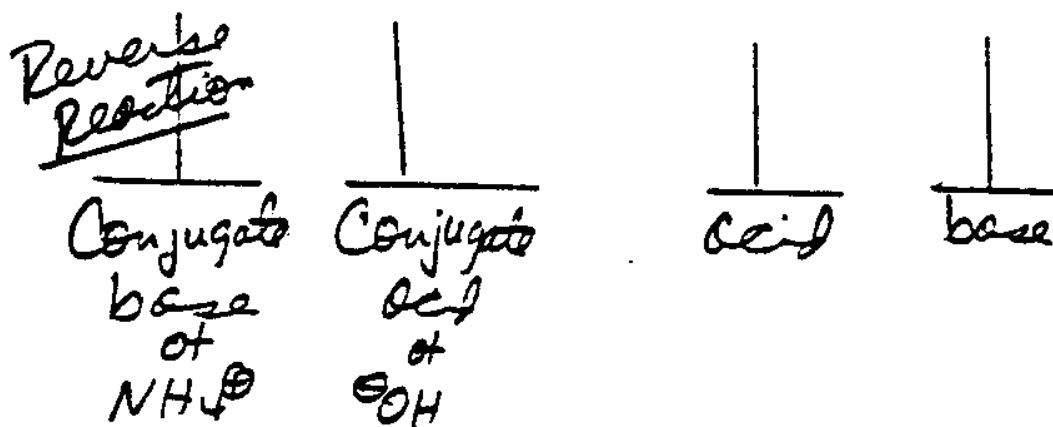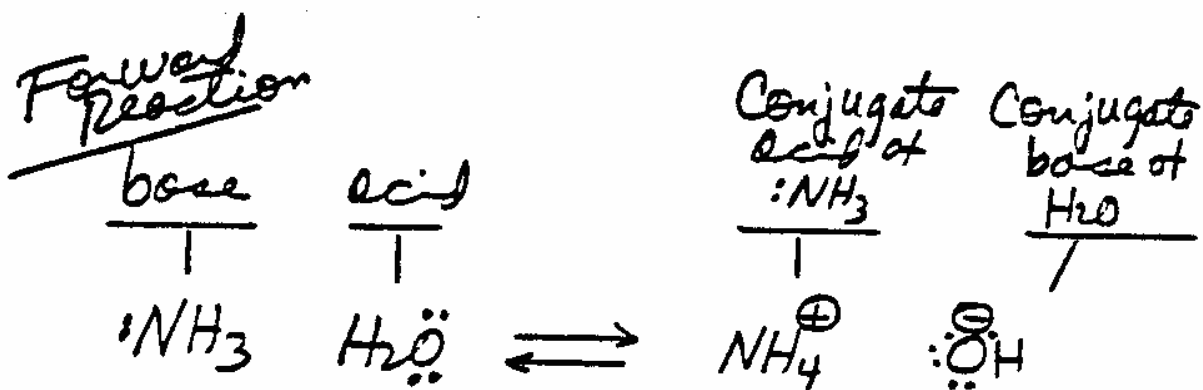
Since the concentrations of NH_4^+ (or RNH_3^+), ^-OH, and H_3O^+ at equilibrium are all relatively low, NH_4^+ (or RNH_3^+) loses a proton to become NH_3 (or RNH_2) primarily by way of its reaction with H_2O (reaction 2).

The Strengths of Bases. The relative amounts of the base $R\text{-}NH_2$ and its conjugate acid $R\text{-}NH_3^+$ that are present at equilibrium in water depend on the **base strength** of $R\text{-}NH_2$. The greater the base strength of an amine $R\text{-}NH_2$, the greater the amount of $R\text{-}NH_2$ in water that is converted to $R\text{-}NH_3^+$, and the greater the value of the equilibrium concentration ratio $[R\text{-}NH_3^+]/[R\text{-}NH_2]$.

For example, if the *base strength* of one amine $R\text{-}NH_2$ is greater than that of some other amine with a different R group ($R'\text{-}NH_2$), then the equilibrium concentration ratio $[R\text{-}NH_3^+]/[R\text{-}NH_2]$ will be greater than the equilibrium concentration ratio $[R'\text{-}NH_3^+]/[R'\text{-}NH_2]$ in water solutions of these two amines. [graphic 3.57]   Water protonates a greater fraction of the stronger base ($R\text{-}NH_2$) then of the weaker base ($R'\text{-}NH_2$).

The Strengths of the Conjugate Acids of these Bases. The ratio $[R\text{-}NH_3^+]/[R\text{-}NH_2]$ not only reflects the *base strength* of $R\text{-}NH_2$, but it also reflects the **acid strength** of $R\text{-}NH_3^+$. When $[R\text{-}NH_3^+]/[R\text{-}NH_2]$ is greater than $[R'\text{-}NH_3^+]/[R'\text{-}NH_2]$, this means that $R\text{-}NH_3^+$ is a *weaker acid* than $R'\text{-}NH_3^+$. It is very important for you to undersatnd that the ratios $[R\text{-}NH_3^+]/[R\text{-}NH_2]$ and $[R'\text{-}NH_3^+]/[R'\text{-}NH_2]$ equally reflect both the *relative basicities* of $R\text{-}NH_2$ and $R'\text{-}NH_2$ and the *relative acidities* of $R\text{-}NH_3^+$ and $R'\text{-}NH_3^+$. [graphic 3.58]

The Relation Between Strengths of Conjugate Acids and Bases. *There is a quantitative relationship between the acid strength of an aminium ion ($R\text{-}NH_3^+$) and the base strength of its amine ($R\text{-}NH_2$).* When a change of R causes the *base* strength of $R\text{-}NH_2$ to *increase,* the *acid* strength of $R\text{-}NH_3^+$ *decreases*, and *vice-versa*. This inverse relationship between the strength of a *base* and the strength of its *conjugate acid* applies to all conjugate acid/base pairs. One can exactly calculate the strength of any base from the strength of its conjugate acid and *vice-versa*.

Because of this quantitative relationship between acidity and basicity, organic chemists and biochemists express the *base strength* of any base (such as $R\text{-}NH_2$) in terms of the *acid strength* of its conjugate acid ($R\text{-}NH_3^+$). In order to prepare to consider this relationship between basicity and acidity in more detail, we will use aminium ions ($R\text{-}NH_3^+$) to first illustrate how we quantitatively describe the *acid strength* of an acid.

3.57   R-ÑH₂   In   R-NH₃⊕
       (base   equilibrium   (acid
        form)   in   form)
                        water
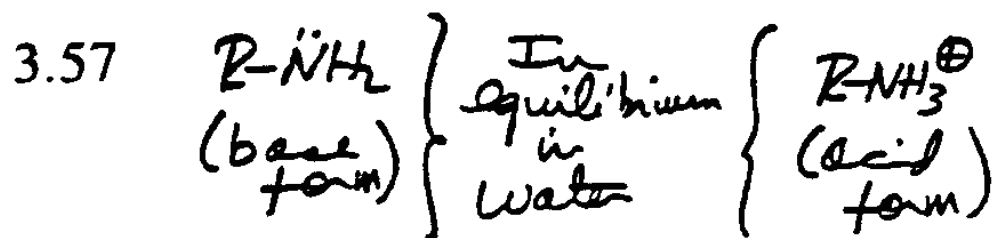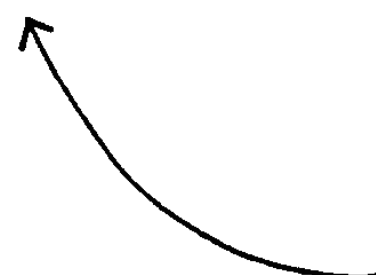
       Increase in
       base strength
       of R-NH₂ shift
       equilibrium
       towards R-NH₃⊕

Result   [R-NH₃⁺]/[R-ÑH₂]   increases
   is

3.58   R-ÑH₂   In   R-ÑH₃⊕
       (base   equilibrium   (acid
        form)   in   form)
                        water
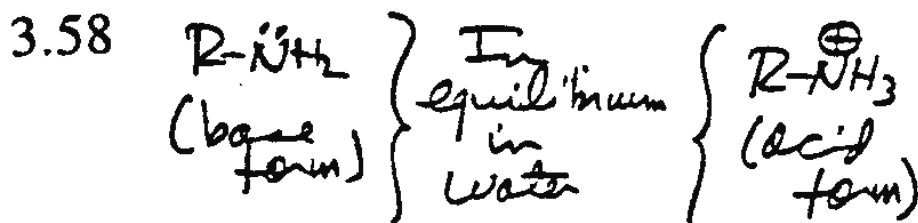
                       Increase in
                       acid strength
                       of R-NH₃⊕ shift
                       equilibrium
                       towards R-NH₂

Result   [R-NH₃⁺]/[R-ÑH₂]   decreases
   is

Aminium Ion Acidity (3.6C)

We can prepare aminium ions (R-NH$_3$$^+$) as ionic compounds (salts) by allowing amines to react with strong acids.

Methanaminium Chloride. *Methanaminium chloride* (CH$_3$NH$_3$$^+$ Cl$^-$) precipitates from organic solvents in which we allow *methanamine* to react with gaseous HCl. [graphic 3.59] We can also isolate *methanaminium chloride* by evaporating the water from an aqueous solution in which we have allowed *methanamine* to react with hydrochloric acid (HCl in water). If we redissolve *methylaminium chloride* in pure water, it acts as an acid and a portion of the methaniminium ion protonates water to give an equilibrium mixture containing H$_3$O$^+$ and CH$_3$NH$_2$, as well as CH$_3$NH$_3$$^+$ and H$_2$O. [graphic 3.60]

Water Can be an Acid or a Base. Remember that water acts both as an acid and a base! In pure water there is always a low concentration of both H$_3$O$^+$ and $^-$OH due to the acid-base reaction between water molecules called **autoprotolysis**. [graphic 3.61] The water molecule accepting the proton is acting as a base while that donating the proton is acting as an acid.

When another base (B:) is added to water, the concentration of $^-$OH increases because water acting as an <u>acid</u> donates protons to B:. [graphic 3.62] Alternatively, when an acid (H-A) is placed in water, the concentration of H$_3$O$^+$ increases because water acting as a <u>base</u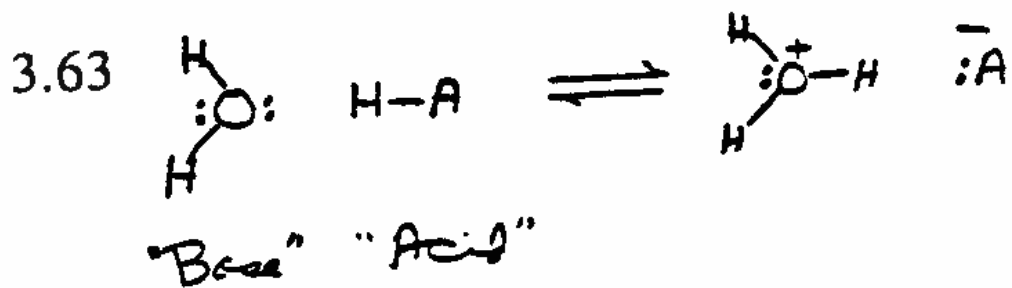> accepts a proton from HA. [graphic 3.63] While both H$_3$O$^+$ and $^-$OH are always present in water, their relative concentrations at equilibrium need not be equal. However they must obey the relationship [H$_3$O$^+$][$^-$OH] = 1 x 10^{-14} = K$_W$ (at 25°C).

Acid Strength of Aminium Ions. The *acid* strength of an *aminium* ion such as CH$_3$NH$_3$$^+$, determines the extent that it reacts with H$_2$O to form H$_3$O$^+$ (and CH$_3$NH$_2$). The equilibrium constant **K** for the resulting equilibrium mixture of CH$_3$NH$_3$$^+$ and CH$_3$NH$_2$ in water directly reflects the acid strength of CH$_3$NH$_3$$^+$. [graphic 3.64] As a result, this equilibrium constant *K* is a measure of the extent to which CH$_3$NH$_3$$^+$ reacts with water to form CH$_3$NH$_2$.

In the same way, the equilibrium constants (K) for water solutions of all acids reflect the strengths of those acids. [graphic 3.65] The acidity of any acid (HA) in water results from the establishment of an equilibrium between it and its conjugate base. The K value for that equilibrium directly measures the position of that equilibrium (the equilibrium concentrations of all species present).

3.59

$$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: \quad H-\ddot{\ddot{C}l: \quad \longrightarrow \quad CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}}}-H \quad :\ddot{\ddot{C}l:^-$$

3.60

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}l:^{\ominus} \quad CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{N}}}-H \quad :\overset{\displaystyle H}{\underset{\displaystyle H}{O}} \quad \rightleftharpoons \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}l:^{\ominus} \quad CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: \quad H-\overset{\oplus}{\overset{\displaystyle H}{O}}\overset{\displaystyle H}{\underset{\displaystyle H}{}}$$

3.61

$$\overset{\displaystyle H}{\underset{\displaystyle H}{}}\ddot{O}: \quad H-\ddot{O}-H \quad \rightleftharpoons \quad \overset{\displaystyle H}{\underset{\displaystyle H}{}}\overset{+}{O}-H \quad \ddot{\ddot{O}}-H^-$$

"Base"   "Acid"

3.62

$$B: \quad H-\ddot{O}-H \quad \rightleftharpoons \quad \overset{+}{B}-H \quad :\ddot{O}-H^-$$

"Base"   "Acid"

3.63

$$\overset{\displaystyle H}{\underset{\displaystyle H}{}}:\overset{\cdot\cdot}{O}: \quad H-A \quad \rightleftharpoons \quad \overset{\displaystyle H}{\underset{\displaystyle H}{}}\overset{+}{O}-H \quad :A^-$$

"Base"   "Acid"

3.64

$$CH_3\overset{\oplus}{NH_3} + H_2\ddot{O} \rightleftharpoons CH_3\ddot{N}H_2 - H_3\overset{\oplus}{O}$$

$$K = \frac{[CH_3\ddot{N}H_2][H_3\overset{\oplus}{O}]}{[CH_3NH_3^+][H_2\ddot{O}]}$$

3.65

$$H_2\ddot{O} + HA \rightleftharpoons H_3\overset{+}{O} + A\overset{-}{:}$$

$$\rightleftharpoons$$

$$HA + H_2\ddot{O} \rightleftharpoons A\overset{-}{:} + H_3\overset{+}{O}$$

$$K = \frac{[H_3\overset{+}{O}][A\overset{-}{:}]}{[H_2\ddot{O}][HA]}$$

3.66

$$K = \frac{[H_3\overset{+}{O}][A\overset{-}{:}]}{[H_2\ddot{O}][HA]}$$

$$\rightleftharpoons$$

$$K \cdot [H_2\ddot{O}] = \frac{[H_3\overset{+}{O}][A\overset{-}{:}]}{[HA]} \equiv K_a$$

Some K Values for Acids in Water. We compare the approximate K value for $CH_3NH_3^+$
in water with those of a number of other acids in Table 3.14. These acids are listed in order
of *decreasing* acid strength so their **K** values become smaller as we proceed down the column
from HCl to H_2O. The K value for $CH_3NH_3^+$ shows that it is a weaker acid than all of these
acids except the weak acid H_2O.

Table 3.14. Approximate Equilibrium Constants for Some Acids in Water

Acid	K
HCl	$\gg 1$
H_2S	10^{-4}
HNO_2	10^{-5}
HF	10^{-5}
H_2CO_3	10^{-8}
NH_4^+	10^{-11}
HCN	10^{-11}
$CH_3NH_3^+$	**10^{-12}**
H_2O	10^{-18}

K_a versus K Values for Aminium Ions. The *K* values in Table 3.14 describe the behavior
of these acids in <u>dilute</u> water solutions where the number of moles of H_2O is much <u>greater</u>
than the number of moles of added acid. Under these conditions, the concentration of water
$[H_2O]$ does not change significantly when it undergoes reaction with HA. For this reason, it
is customary to factor out $[H_2O]$ and to express acid strengths using **acidity constants (K_a)**
listed in Table 3.15 [next page] rather than the K values in Table 3.14. [graphic 3.66]

Since chemists define K_a values as $K \cdot [H_2O]$, they are larger than K values by the factor 55.5
that is the value for $[H_2O]$ in mol/L. The pK_a values in Table 3.15 are quantitatively related
to the K_a values. We discuss them later in this section and review their relation to K_a values.

Table 3.15. K_a and pK_a Values for Various Acids in Water

Acid	K_a	pK_a
HCl	$\gg 1$	$\ll 1$
H_2S	1×10^{-2}	2.0
HNO_2	5×10^{-4}	3.3
HF	4×10^{-4}	3.5
H_2CO_3	4×10^{-7}	6.4
NH_4^+	6×10^{-10}	9.3
HCN	5×10^{-10}	9.3
$CH_3NH_3^+$	**3×10^{-11}**	**10.6**
H_2O	2×10^{-16}	15.7

K_a Values Measure both Acidity and Basicity. We show the K_a expression for an aminium ion RNH$^+$ in Figure [graphic 3.67] . [graphic 3.67]   A particularly useful form of this K_a expression shows that the concentration ratio [R-NH$_2$]/[R-NH$_3$$^+$] depends only on the value of K_a for RNH$_3$$^+$, and on the equilibrium value of [H$_3$O$^+$].

The ratio [R-NH$_2$]/[R-NH$_3$$^+$] is the ratio of *[base form]/[acid form]* for the R-NH$_2$ and R-NH$_3$$^+$ conjugate base-acid pair, and its dependence on K_a and [H$_3$O$^+$] can be extended to any equilibrium between a conjugate acid and base in water. [graphic 3.68]   As a result, the K_a of any acid (its acid strength), and the [H$_3$O$^+$] for its water solution, uniquely determine the relative amounts of *base* <u>and</u> *acid* forms of any conjugate acid/base pair.

Since we saw earlier that the ratio *[base form]/[acid form]* also depends on the *basicity* of the base form, a quantitative relationship must exist between *basicity* of the *base form* <u>and</u> *acidity* of the *acid form*. As a result, K_a values for acids (Table 3.16 [next page]) reflect not only the relative strengths of those acids, but also the relative strengths of their conjugate bases.

For the nine acids included in Table 3.16, HCl is the strongest acid (greatest K_a value) and it has the weakest conjugate base (Cl$^-$). The weakest acid shown in Table 3.16 is H$_2$O (smallest K_a value) and it has the strongest conjugate base (OH$^-$). In a comparison of any *two acids*, the one with the *higher K_a* value is the *stronger acid*. In contrast, when we compare any *two bases*, that with the *higher K_a* value <u>for its conjugate acid</u> is the *weaker of the two bases*.

Table 3.16. Some Acids, their Conjugate Bases, and K_a Values.

Acid	K_a	Strength of Acid	Conjugate Base	Strength of Base
HCl	>>1	**Strongest**	Cl$^-$	**Weakest**
H$_2$S	1×10^{-2}		HS$^-$	
HNO$_2$	5×10^{-4}		NO$_2$$^-$	
HF	4×10^{-4}		F$^-$	
H$_2$CO$_3$	4×10^{-7}		HCO$_3$$^-$	
NH$_4$$^+$	6×10^{-10}		NH$_3$	
HCN	5×10^{-10}		CN$^-$	
CH$_3$NH$_3$$^+$	3×10^{-11}		CH$_3$NH$_2$	
H$_2$O	2×10^{-16}	**Weakest**	OH$^-$	**Strongest**

3.67 $R-\overset{+}{N}H_3 + H_2\ddot{O} \rightleftharpoons R-\ddot{N}H_2 + H_3\overset{+}{O}$

$$K_a = \frac{[R-\ddot{N}H_2][H_3O^+]}{[R-NH_3^+]}$$

or

$$\frac{[R-\ddot{N}H_2]}{[R-NH_3^+]} = \frac{K_a}{[H_3O^+]}$$

3.68 $\underset{\text{Form}}{\text{Acid}} + H_2\ddot{O} \rightleftharpoons \underset{\text{Form}}{\text{Base}} + H_3O^+$

$$K_a = \frac{[\text{Base Form}][H_3O^+]}{[\text{Acid Form}]}$$

or

$$\frac{[\text{Base Form}]}{[\text{Acid Form}]} = \frac{K_a}{[H_3O^+]}$$

An Equilibrium Calculation. K_a expressions permit quantitative calculations of acid and conjugate base concentrations for equilibrium mixtures of weak acids in water. Such a calculation shows that a solution prepared by disolving 0.1 mol $CH_3NH_3^+$ in sufficient water to give 1.0 L of solution has equilibrium values of 2 x 10^{-5} for $[CH_3NH_2]/[CH_3NH_3^+]$ and 2 x 10^{-6} M for $[H_3O^+]$. Since the number of moles of H_2O protonated by $CH_3NH_3^+$ corresponds to the number of moles of CH_3NH_2 present, the very small $[CH_3NH_2]/[CH_3NH_3^+]$ ratio shows that the amount of H_2O protonated by $CH_3NH_3^+$ to give H_3O^+ and CH_3NH_2 is so small that the value of $[H_2O]$ in this solution is virtually identical to $[H_2O]$ in pure water.

K_a and pK_a Values. Chemists usually discuss acid strengths in terms of pK_a values (Table 3.15) that they calculate from K_a values according to either of the two mathematically equivalent relationships shown here.

$$pK_a \ = \ -\log_{10}K_a \qquad or \qquad K_a \ = \ 10^{-pK_a}$$
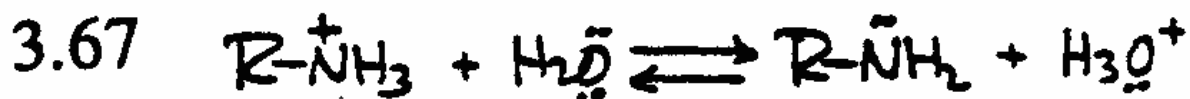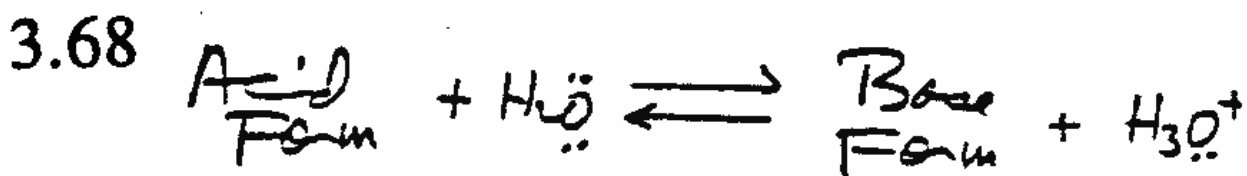
You may be more familiar with the first equation, but the second equation is particularly useful since it shows a way to determine *approximate* pK_a values from K_a values without using a calculator. Let's illustrate this *approximate* method for $CH_3NH_3^+$ that has a K_a value of 2.7 x 10^{-11}.

(1) We can calculate the precise pK_a value of 10.6 for $CH_3NH_3^+$ by substituting $K_a =$ 2.7 x 10^{-11} into either equation shown above and solving for pK_a using a calculator.

(2) In contrast, if we *approximate* K_a as 10^{-11} and substitute that value in our second equation, we obtain the relationship $10^{-11} = 10^{-pK_a}$. By inspection we see that the corresponding *approximate* pK_a is 11. For many purposes, this approximate pK_a value of 11 for $CH_3NH_3^+$ is just as useful as the precise value of 10.6.

We can use this approximation procedure for any acid. If we write the K_a of the acid as *a x 10^{-b}* (where $1 < a < 10$), then *b* is an approximate pK_a value. This value of *b* may be slightly larger than the true pK_a, but it is always within 1 pK unit of pK_a since $(b-1) < (pK_a) < b$ (see Table 3.15).

Effects of R on R-NH_3^+ Acidity and R-NH_2 Basicity. When the R group of R-NH_2 is alkyl or cycloalkyl, the actual structure of this R group usually has only a small effect on the basicity of R-NH_2 as shown by the similar K_a (or pK_a) values for several different aminium ions (R-NH_3^+) (Table 3.17).

Table 3.17. K_a and pK_a Values for Various Alkanaminium Ions (RNH_3^+).

Alkanaminium Ion	K_a	pK_a
$(CH_3)_3CCH_2\text{-}NH_3^+$	7.1×10^{-11}	10.2
$CH_3\text{-}NH_3^+$	2.7×10^{-11}	10.6
cyclohexyl-NH_3^+	2.2×10^{-11}	10.7
$CH_3CH_2\text{-}NH_3^+$	1.6×10^{-11}	10.8
$(CH_3)_3C\text{-}NH_3^+$	1.5×10^{-11}	10.8

These K_a values fall in the narrow range of $(1.5$ to $7.1)$ x 10^{-11} in contrast to those in Table 3.15 that vary over eleven powers of ten (10^{11}) for the wide variety of acids in that series. Since the effect of changes in R on aminium ion acidity is generally small, so is the effect of these changes on the basicity of the corresponding bases (R-NH_2).

Comparative Basicities of 1°, 2°, and 3° Amines. We have been focusing on 1° amines, but the basicities of similar 2° and 3° amines are comparable since the acidities of their aminium ions (Table 3.18) are so similar.

Table 3.18. Comparative K_a Values for Some 1°, 2°, and 3° Aminium Ions

Aminium Ion*		K_a	pK_a
$MeNH_3^+$	(1°)	2.7×10^{-11}	10.7
$Me_2NH_2^+$	(2°)	1.9×10^{-11}	10.7
Me_3NH^+	(3°)	1.6×10^{-10}	9.8
$EtNH_3^+$	(1°)	1.6×10^{-11}	10.8
$Et_2NH_2^+$	(2°)	3.2×10^{-11}	10.5
Et_3NH^+	(3°)	9.8×10^{-12}	11.0

* Me = methyl = CH_3, and Et = ethyl = CH_3CH_2

Effects of Structure on Amine Basicity. In Table 3.18, the pK_a value for Me_3NH^+ (3°) is slightly lower than those for $MeNH_3^+$ (1°) and $Me_2NH_2^+$ (2°). In contrast the pK_a value for Et_3NH^+ (3°) is slightly higher than those for $EtNH_3^+$ (1°) and $Et_2NH_2^+$ (2°). These differences between R = methyl and R = ethyl are due to a combination of effects including how methyl and ethyl groups (1) affect water solvation of aminium ions and amines, and (2) interact "electronically" with their attached N. We will discuss these types of structural effects (**substituent effects**) on chemical and physical properties in Chapter 14.

Basicity of Alcohols and Ethers (3.6D)

While organic chemists usually do not think of alcohols (ROH) and ethers (ROR) as organic bases, very strong acids will protonate their O atoms.
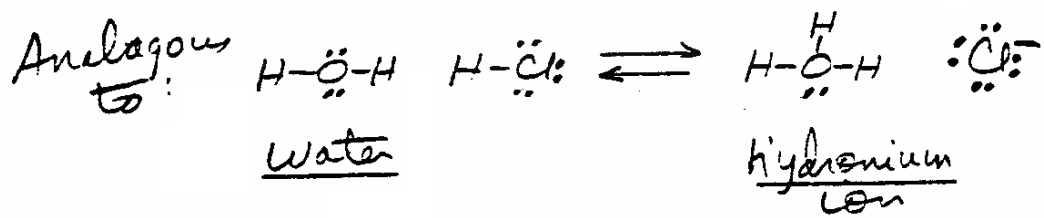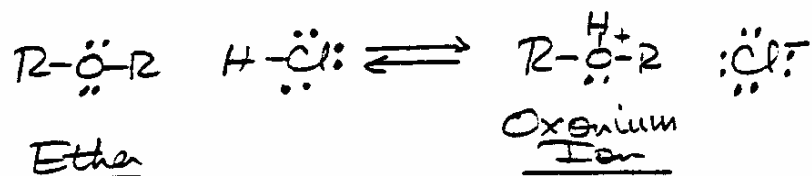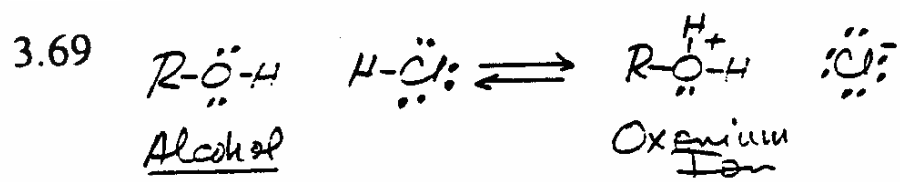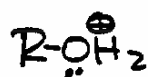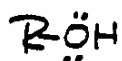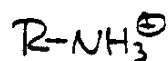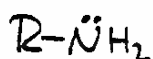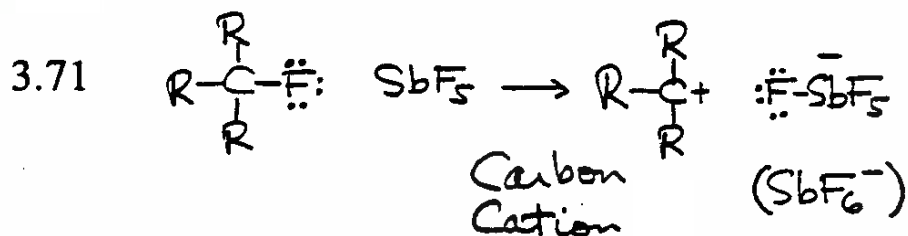
Oxonium Ions. Protonation of alcohols or ethers by strong acids gives **oxonium ions** that are analogous to *hydronium ions* formed by protonation of water. [graphic 3.69] Protonation of an unshared electron pair on oxygen of ROH or ROR to give an *oxonium* ion is analogous to protonation of an unshared electron pair on nitrogen of an amine to give an *aminium* ion. However, oxonium ions are much stronger acids than aminium ions. K_a values for simple *oxonium* ions are 10^{+2} or larger compared to K_a values of 10^{-11} for *aminium* ions.

Because of the inverse relationship between strengths of acids and those of their conjugate bases, the high acidity of an *oxonium ion* and low acidity of an *aminium ion* correlate with the low basicity of *alcohols* and *ethers* and the much higher basicity of *amines*. [graphic 3.70] In spite of the fact that alcohols and ethers are only very weak bases, we will see later that *oxonium ions* are important intermediates in many chemical reactions involving alcohols or ethers in strongly acidic solutions.

Basicity of Haloalkanes (3.6E)

Halogen atoms (X) in haloalkanes (R-X) also have unshared electron pairs (like N in amines and O in alcohols and ethers), but they are not protonated even by acids as strong as HCl or H_2SO_4. This indicates a relative basicity order $R_3N \gg$ (R-OH and R-OR) $\gg$ R-X that parallels the relative positions of N, O, and the halogens (X) in the periodic table. The complete absence of measurable basicity for haloalkanes (R-X) is consistent with this order and the observation that aminesw are at least 10^{13} times <u>more</u> basic than alcohols and ethers.

Super Acids. There are highly electron deficient reagents besides proton donating acids that react with unshared electron pairs on halogen atoms of haloalkanes, as well as with unshared electron pairs on alcohols, ethers, and amines. One example is SbF_5 (antimony pentafluoride) which causes the very strong C-F bond to break leading to the formation of species with positively charged carbon (carbon cations). [graphic 3.71] SbF_5 is called a **super acid** because it reacts with unshared electron pairs even on very weakly basic atoms such as F. We will discuss this type of reaction, and the resultant carbon cations formed as products, in a later chapter. Professor George Olah, University of Southern California, won the 1994 Nobel prize in chemistry for discovering this and related reactions.

3.69 $R-\ddot{O}-H$ $H-\ddot{\underset{\cdot\cdot}{Cl}}: \rightleftharpoons$ $R-\overset{H}{\underset{\cdot\cdot}{O}}{}^{+}-H$ $:\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$

<u>Alcohol</u>   <u>Oxonium Ion</u>

$R-\ddot{O}-R$ $H-\ddot{\underset{\cdot\cdot}{Cl}}: \rightleftharpoons$ $R-\overset{H}{\underset{\cdot\cdot}{O}}{}^{+}-R$ $:\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$

<u>Ether</u>   <u>Oxonium Ion</u>

<u>Analogous to</u>: $H-\ddot{O}-H$ $H-\ddot{\underset{\cdot\cdot}{Cl}}: \rightleftharpoons$ $H-\overset{H}{\underset{\cdot\cdot}{O}}-H$ $:\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$

<u>Water</u>   <u>Hydronium Ion</u>

3.70

<u>Oxonium Ion</u>	<u>Alcohol</u>
$R-\overset{\oplus}{\underset{\cdot\cdot}{O}}H_2$	$R-\ddot{O}H$
$\dfrac{K_a \simeq 10^{+2}}{\text{Strong Acid}}\Big\}$	Weaker Base than $R-\ddot{N}H_2$
<u>Aminium Ion</u>	<u>Amine</u>
$R-NH_3^{\oplus}$	$R-\ddot{N}H_2$
$\dfrac{K_a \simeq 10^{-11}}{\text{Weak Acid}}\Big\}$	Stronger Base than $R-\ddot{O}H$

3.71 $R-\overset{R}{\underset{R}{C}}-\ddot{\underset{\cdot\cdot}{F}}:$ $SbF_5 \longrightarrow R-\overset{R}{\underset{R}{C}}{}^{+}$ $:\ddot{\underset{\cdot\cdot}{F}}-\bar{SbF}_5$

<u>Carbon Cation</u> (SbF_6^{-})

Chapter Review

Halogen, OH, and NH2 Substituent Groups. (1) Replacement of an H in an alkane (RH) by groups with N, O, or halogen atoms leads to molecules such as **haloalkanes** (**RX**), **alcohols** (**ROH**), and **amines** (**RNH$_2$**) with distinctly different properties. (2) N, O, and X are more **electronegative** than C so their bonds to C are polar [(δ+)C-X(δ-), (δ+)C-O(δ-), and (δ+)C-N(δ-)] with **dipole moments**. (3) In their compounds, C, N, O, and X have 4, 3, 2, and 1 chemical bonds, and 0, 1, 2, and 3 unshared electron pairs.

Haloalkanes (R-X). (1) Haloalkanes are named like branched alkanes. (2) Halogen electronegativity order is F > Cl > Br > I so that C-X polarity decreases in the same order. (3) C-X **bond length** order is C-I > C-Br > C-Cl > C-F while **bond strength** order is C-F > C-Cl > C-Br > C-I. (4) Halogen "size" order is I > Br > Cl > F, but effective size also depends on C-X bond length.

Alcohols (R-OH). (1) Replacement of one H in water (HOH) by R gives alcohols (ROH) named as **alkanols** or substituted alkanols. (2) C-O-H bond angles are tetrahedral. (3) Bond polarity in alcohols is (δ$^+$)C-O(δ$^-$) and (δ$^-$)O-H(δ$^+$). (4) Alcohol O-H groups form **hydrogen bonds** that have a dramatic effect on their properties.

Ethers (ROR). (1) Replacement of H on ROH by R gives **ethers** (ROR) named **alkoxyalkanes**, while cyclic ethers are **oxacycloalkanes**. (2) Bond angles at O of ethers are larger than those of alcohols, but they are approximately tetrahedral. (3) Ethers cannot form hydrogen bonds with themselves so their properties are distinctly different from those of alcohols. (4) They serve as polar solvents without OH groups for certain polar compounds.

Amines (R-NH2, R2NH, and R3N). (1) Replacement of H by R on NH$_3$ gives RNH$_2$ (1° amines), R$_2$NH (2° amines), or R$_3$N (3° amines). (2) 1° amines are **alkanamines**, 2° and 3° amines are **N-alkylalkanamines**, and cyclic amines are **azacycloalkanes**. (3) Bond angles at N are tetrahedral so amines are **pyramidal** and rapidly **invert**. (4) C-N and N-H bonds are polar like C-O and O-H bonds, but N-H hydrogen bonding is not as strong as that for O-H. (5) C-N, C-O, and C-C bond lengths are about 1.5 Å while N-H, O-H, and C-H bond lengths are about 1Å. (6) N-H, O-H, and C-H bonds are stronger than C-N, C-O, and C-C bonds.

Amines as Bases. (1) Amines (R$_3$N) are **bases** and react with proton donors (acids) to form their conjugate acid aminium ions (R$_3$NH$^+$). (2) Because amine base strength is proportional to aminium ion acid strength, **K$_a$** and **pK$_a$** values for aminium ions are used to express amine base strength. (3) Alcohols are much less basic than amines, but react with strong acids to form oxonium ions while haloalkanes are not basic.