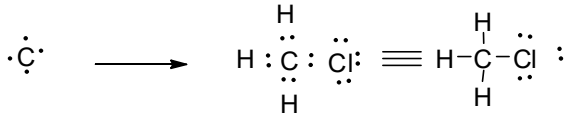
Organic Chemistry 1: Introductory Review Handout

*This handout contains a synopsis of material that you should already know from General Chemistry. These topics will be applied throughout this Organic Chemistry course. If you are not familiar with these, please review them in Klein's Ch. 1 and some of Ch. 2, and/or ask for help!

Big picture: We are starting with a lot of background information that can seem disconnected from applications. This will form the basis of future discussions. These concepts will come back and be put in the context of physical properties or reactions. Discussing the concepts absent a context can make it more difficult, however you should have seen most of these concepts before in Gen Chem. Note: we do grab different concepts at different times to understand particular chemical behavior. There is no nice organized, cohesive understanding that explains all chemical behavior. The concepts are sometimes overlapping and interconnected, but you will find different ideas rolled out on different occasions to explain a particular behavior.

I. Organic Structure Bonding and Depictions of Molecules: What do all those lines and dots mean?

A. Lewis dot structures (Klein 1.2, 1.3)

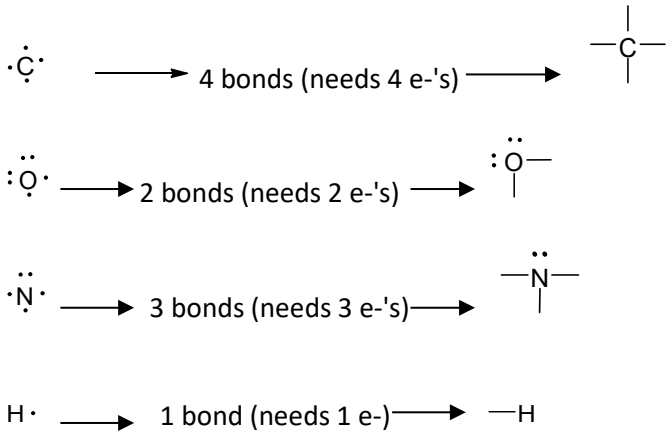


$2s^2 2p^2$ Valence shell

Why did C form additional bonds?
Octet Rule: Complete the outer shell! Become like the noble gases!

B. Generalizations with Lewis dot structures
- C, O, N, H ~ 95% of organic chemistry course

Generalizations with C, H, N and O

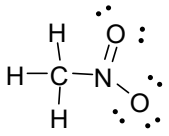
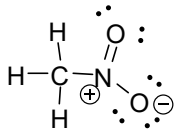


C. Formal charge calculations (Klein 1.4, 2.4, 2.5, 2.9)
-a way of determining the "mental state" of an atom: Is this atom stable (happy) or unstable (unhappy)?

1. formal charge= (no. of valence e-'s) – (no. of nonbonding e-'s) – (no. of bonds)

C always 4 valence e-'s
H always 1 valence e-
N → 5
O→ 6

2. example: CH_3NO_2

	f.c. calcuations C=4-0-4= 0 H=1-0-1=0 =O =6-4-2=0 -O =6-6-1= -1 N=5-0-4= +1	

-alternative example: zwitterion of an amino acid such as alanine, glycine, tyrosine or proline.

3. Generalizations…

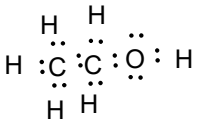
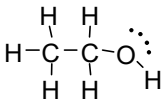
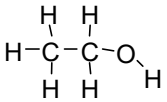
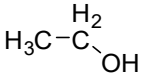
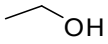
atom	bonds/lone pairs	charge
C	4/0	0
C	3/0	+1
C	3/1	-1
O	2/2	0
O	3/1	+1
O	1/3	-1
N	3/1	0
N	4/0	+1
N	2/2	-1 (rare)
H	1/0	0
H	2/0	Get out of this course!

-By periodicity trends, S will be like O; P will be like N; S and P have d orbitals so sometimes they will add bonds with d orbitals

-Halides are mostly 1 bond and 3 lone pairs; occasionally they will have two bonds and two l.p.'s for a +1 charge

*You need to know these all. You can calculate them each time until you know them or you can memorize them.

D. Complex organic Lewis dot structures abbreviated: (Klein 2.1, 2.2)

1. ethanol….	2. first abbreviation…	3. second abbreviation…	4. most abbreviated…
 (too much work!)	 or  (Lewis structure; called Kekule structures in Bruice)	 (condensed structures)	 (line drawings; called skeletal structure by Bruice)

**YOU MUST BECOME COMFORTABLE RECOGNIZING THESE STRUCTURAL ABBREVIATIONS!

-Key point: C has four bonds, so add the necessary H's to give it four bonds

-line drawings highlight an attitude about structures: most C's don't matter, they are just the framework/scaffolding of organic structures (alkanes don't do any rxns.!)

II. Electrons and Bonding: Where did all the electrons go? (Klein 1.6)

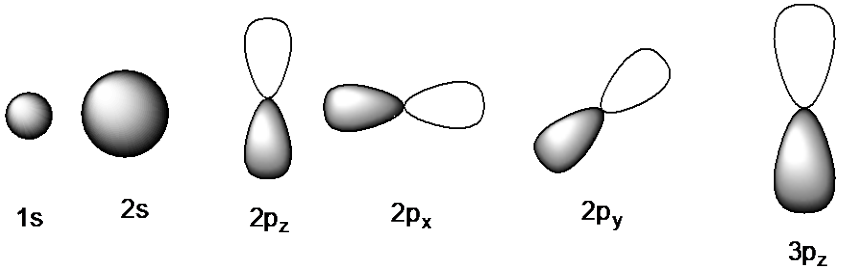
A. Atomic Orbitals

-Bohr/Schrodinger model: $1s^2 2s^2 2p^6$ etc

-electrons occupy discrete energy levels

-within energy levels, the area an electron occupies can vary

-quantum mechanics describes shapes of these regions or orbitals as follows:

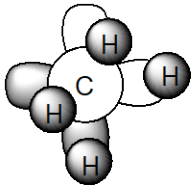


B. Valence Bond Theory/Hybrid Orbitals (Klein 1.7)

-try to apply atomic orbital theory to explain molecular shape and it failed miserably!

-e.g. CH_4

valence e-'s= $2s^2 2p^2$

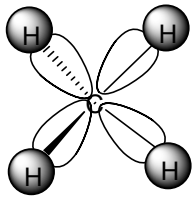


*Theory predicts: some bond angles of 90° and H's in different positions around C

Reality: H's distributed equally around C and with uniform bond angles of 109.5°

Conclusion: Atomic orbitals don't explain bond angles well!

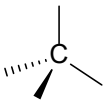
-Solution: Make superbonds! Hybrid orbitals (Klein 1.9)
$2s + 2p_x + 2p_y + 2p_z = 4\ sp^3$ orbitals (1 x 2s orbital + 3 x 2p orbitals)



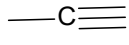
4 H's equally distributed and spaced around C! Explains reality!
(note: technically each sp^3 hybrid orbital has a tiny little orbital on the opposite side of the large orbital)

C. Atomic and Molecular shape (Klein 1.10)
-based on hybridization of orbitals…

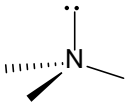
<u>C shapes:</u>

-C with four single bonds  → tetrahedral (sp^3)

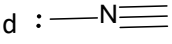
-C with one double bond and two single bonds  → trigonal planar (sp^2)

-C with one triple bond and one single bond  → linear (sp)

<u>N shapes:</u>

-N with three single bonds  → trigonal pyramidal (sp^3)

-N with one double bond and two single bonds  → trigonal planar (sp^2)

-N with one triple bond  → terminal (can't be detected)

<u>O shapes:</u>

-O with two single bonds  → bent (sp^3)

-O with one single bond  → terminal (can't be detected)

D. Bond lengths, angles and strengths (Klein 1.9)
-we will return to these ideas to understand molecule properties and rxns.

-sigma=single vs. double=sigma+pi vs. triple=sigma+pi+pi

1. influences on bond length:
a) bond order: single (1.5 A)>double>triple (1.2 A)
b) atom hybridization: sp^3>sp^2>sp
-Comments: *more s character means closer to nucleus (that's based on the shape of the s orbital) and that means shorter bonds and stronger bonds (e-'s are held closer to + nucleus!) [THIS IS A CRITICAL, FREQUENTLY USED RULE/UNDERSTANDING!!]

2. bond angles:
sp^3=109.5
sp^2=120
sp=180

3. influences on bond strength:

a) <u>bond length:</u> longer bond is a weaker bond
e.g.
C-F vs. C-I (2nd period vs. 5th period)
1.39 A's vs. 2.14 A's
481 vs. 243 kJ/mol
*C-F bond has two atoms of the same period and similar size; that makes them have strong overlap in their orbitals and a strong bond.

b) <u>bond order:</u> single (377 kJ/mol, see Bruice Table 1.7!) <double (728 kJ/mol) <triple (967 kJ/mol)
*note: double bond=sigma + pi; triple bond=sigma + pi + pi
-analysis of bond strength is considering all these bonds combined.
-*Individually, the pi will be weaker than the sigma (see next item).*

c) <u>bond type:</u> sigma>pi
H_3C-CH_3, 377 kJ/mol
H_2C=CH_2, 728 kJ/mol
…therefore for H_2C=CH_2, sigma bond=377 and pi bond=351 kJ/mol!
-pi bond in triple is even weaker at 239 kJ/mol
*pi bonds are weaker!
-Think about the structure of the pi bond vs. sigma bond and this makes sense! pi bonds are not held between the positive nuclei, rather they are above and below the plane of the sigma bond. This is a weaker orientation as they cannot be held tightly by the nuclei, so they should be more reactive!

III. Dipole Moments of Bonds and Molecules (Klein 1.5, 1.11)
*critical to understanding molecule's physical properties and some reactivity
<u>Dipole Moment of Bonds</u>= eN + bond length
<u>Dipole Moment of Molecules</u>=cumulative effect of all polar bonds

A. Dipole Moment of Bonds

1. Electronegativity (eN) is key!! (Klein 1.5)

-each atom has a unique electronegativity (Linus Pauling) that describes its ability to attract electrons

-this electronegativity depends on the number of protons and the size of the atom

-important Pauling scale eN's:

C, 2.55

H, 2.20

N, 3.04

O, 3.44

-eN provides the basis for a lot of chemical understanding well beyond dipole moment discussions

*conclusion: O and N will attract more e-'s!! This is critical to their reactivity patterns.

*general pattern: most eN atoms in top right corner of periodic table, starting with F; least eN atoms in lower left corner of periodic table, i.e. francium (Fr) and cesium (Cs)

2. Bond length and dipole moment

*dipole moment is a combination of atom eN and bond length….

-from Bruice Table 2.4, p. 89

bond	eN of halide (C, eN=2.55)	bond length, angstroms	dipole moment, Debyes	bond strength, kJ/mol
C-F	4.0	1.39	1.6	481
C-Cl	3.0	1.78	1.5	350
C-Br	2.8	1.93	1.4	301
C-I	2.5	2.14	1.2	243

B. Dipole moment of Molecules

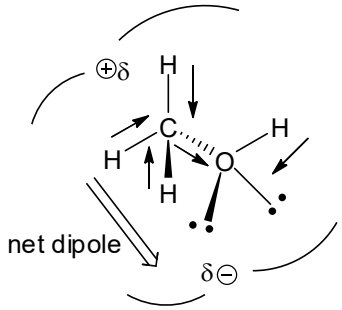
<u>Example:</u> methanol, CH_3OH

1. generate Lewis dot structure

-remember C needs 4 bonds, H one and O two

2. determine dipole moments of bonds primarily using differences in eN

3. analyze cumulative effect of all bond dipole moments to determine molecule's dipole and based on atomic/molecular geometry



C, 2.55; H, 2.20; O, 3.44

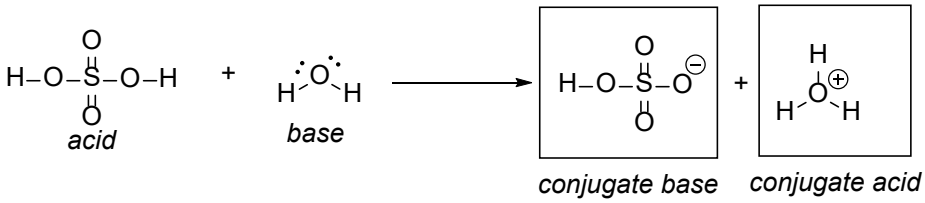
[Note: C has a tetrahedral geometry and O has a bent geometry.]

-methanol is a fairly polar molecule: Little grease (C's and H's), eN O atom present. The analysis is very qualitative not quantitative like Gen Chem!! This is typical of OC.

IV. GC2 concepts

A. pK_a and Acid-base Equilibrium

Example:



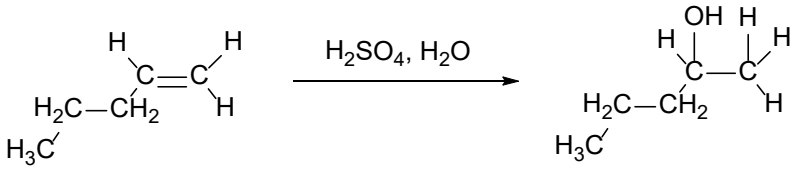
Acid dissociation equilibrium: K_a = [products] / [reactants]
$pK_a = -\log_{10}(K_a)$

Complete reaction equation (fill in boxes) and analyze pKa's:
H_2SO_4 proton pK_a=-5;
H_2O proton pK_a=15.7 (note we are not talking about H_3O^+ and this is not the same as water's pH=7!)

B. Thermodynamics/Thermochemistry

1. enthalpy (ΔH) and free energy (ΔG) of reactions; $\Delta G = \Delta H - T\Delta S$; exergonic and endergonic reactions

2. bond dissociation energies
Example:



<u>Bond Energy analysis for E+ add'n of H_3O^+ to alkene:</u>
$-\Delta H^o = \Sigma$ (bonds broken) – Σ (bonds formed)
=[(C-C pi bond) + (O-H sigma bond)] - [(C-O sigma bond) + (C-H sigma bond)]
=[259 + 497 kJ/mol] - [387 + 423 kJ/mol] = -54 kJ/mol
-therefore slightly exothermic

C. Chemical Kinetics

-1st and 2nd order reactions

A + B → Y + Z

rxn. rate = - Δ [reactant]/ Δ time= k [A] or k [A][B]