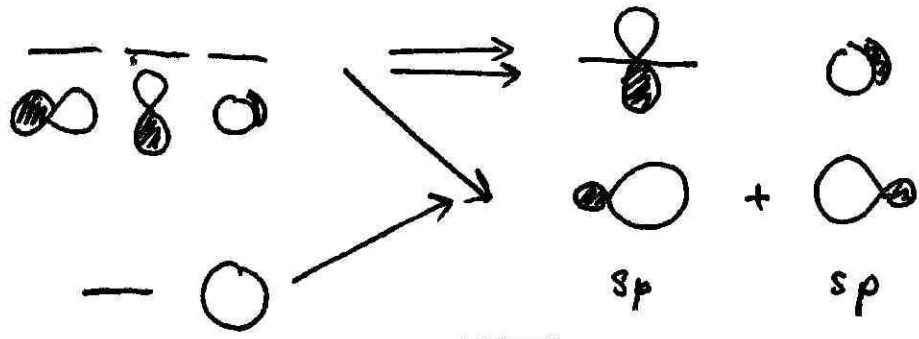
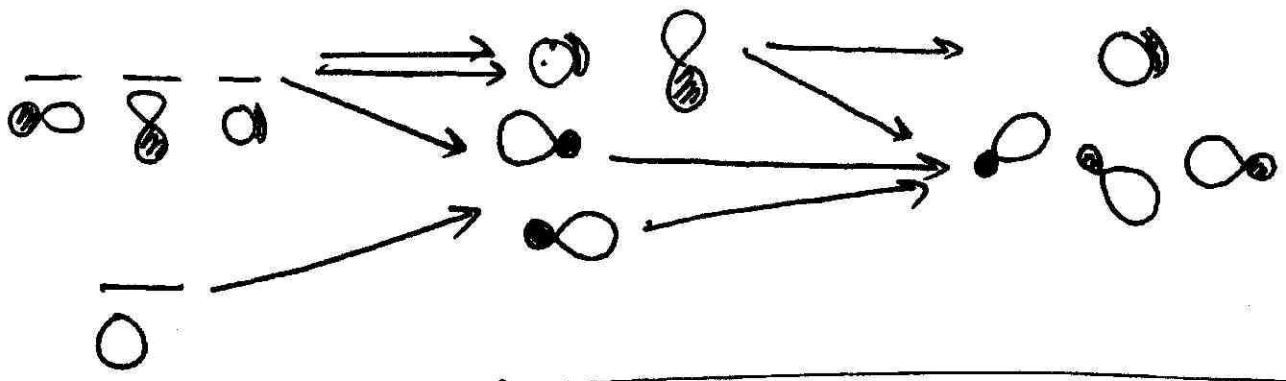


④

sp

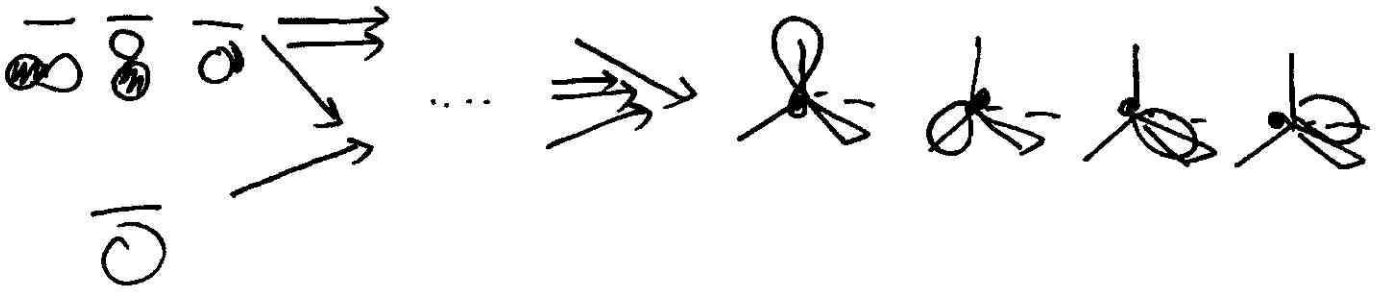


sp²



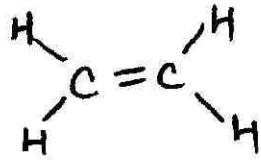
& as we saw before

sp³



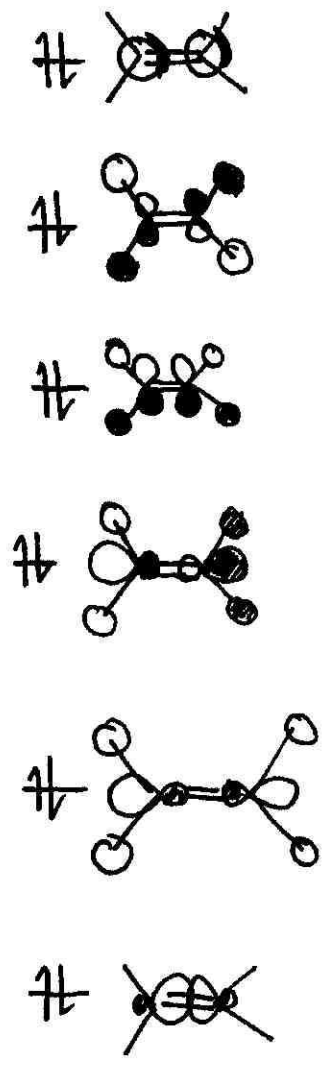
⑤ For all organic molecular MOs it is possible to reduce the MO diagram into localized orbitals based on the sp , sp^2 and sp^3 scheme. We use the sp scheme for two coordinate C, sp^2 for three coordinate C and sp^3 for 4 coordinate C.

I'll give one example: C=C. We consider only the filled MO's

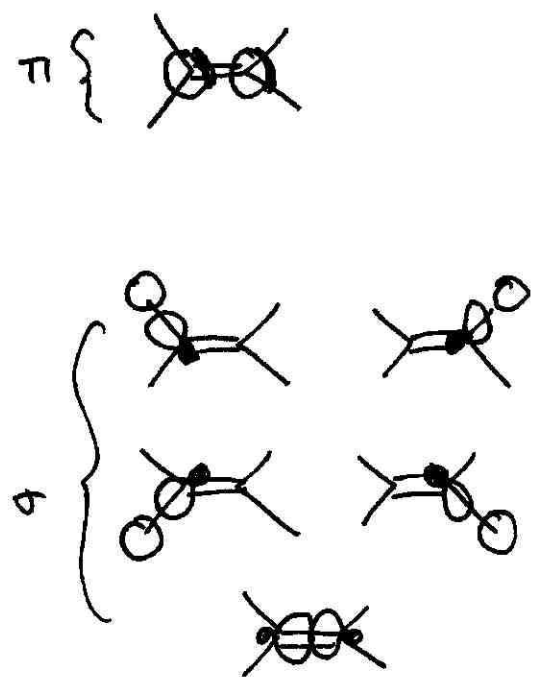


filled MO's

filled localized orbitals

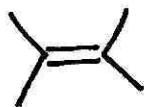


by repeated pairwise mixing we can generate



Note the MO's are measurable states. The 5 σ states are not measurable states (i.e., are not eigenstates of any ordinary measurement).

⑥ What's the use of this localized orbital picture? Not very much that I am aware of. It gives you a quick way of counting the number of σ bonding orbitals.

With the  molecule & sp^2 hybridization on the C, one can generate 5 bonding σ orbitals.

But quite frankly there are just as quick ways to count.

C follows the octet rule. It is not hypervalent. \therefore It has 4 bonds. I can make only one π -bonding MO in ethylene \therefore the other bonding orbitals must be σ . By Lewis structures there are 5 of bonds unaccounted for by the π system.

⑦ The hard-soft concept is much deeper (in my opinion)

⑧ Hard moities are moities which when they come together do so with a strong ionic interaction. Generally the cation is electropositive & the anion is electronegative.

Hard { cations : H^+ , Li^+ , Be^{2+}
acids

Hard { anions : F^- , OH^-
bases

Hard cation & hard anion make ionic bonds

⑨ Soft { cations } { anions } are moities which when they come together, there is a big change in De Broglie wavelengths. Generally the acid is not so electropositive & the base is not so electronegative.

Soft acids : Hg^+ , Pt^{2+} , Au^+

Soft bases : H^- , SR , $C \equiv O$, PR_3

Soft acids & bases make covalent/metallic bonds

⑩ further examples are given on the next page.

Table 7.6 Classification of hard and soft acids

44.1

Hard acids

H^+ , Li^+ , Na^+ , K^+ (Rb^+ , Cs^+)
 Be^{+2} , $Be(CH_3)_2$, Mg^{+2} , Ca^{+2} , Sr^{+2} (Ba^{+2})
 Sc^{+3} , La^{+3} , Ce^{+4} , Gd^{+3} , Lu^{+3} , Th^{+4} , U^{+4} , UO_2^{+2} , Pu^{+4}
 Ti^{+4} , Zr^{+4} , Hf^{+4} , VO^{+2} , Cr^{+3} , Cr^{+6} , MoO^{+3} , WO^{+4} , Mn^{+2} , Mn^{+7} , Fe^{+3} , Co^{+3}
 BF_3 , BCl_3 , $B(OR)_3$, Al^{+3} , $Al(CH_3)_3$, $AlCl_3$, AlH_3 , Ga^{+3} , In^{+3}
 CO_2 , RCO^+ , NC^+ , Si^{+4} , Sn^{+4} , CH_3Sn^{+3} , $(CH_3)_2Sn^{+2}$
 N^{+3} , RPO_2^+ , $ROPO_2^+$, As^{+3}
 SO_3 , RSO_2^+ , $ROSO_2^+$
 Cl^{+3} , Cl^{+7} , I^{+5} , I^{+7}
 HX (hydrogen-bonding molecules)

Borderline acids

Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2}
 Rh^{+3} , Ir^{+3} , Ru^{+3} , Os^{+2}
 $B(CH_3)_3$, GaH_3
 R_3C^+ , $C_6H_5^+$, Sn^{+2} , Pb^{+2}
 NO^+ , Sb^{+3} , Bi^{+3}
 SO_2

Soft acids

$Co(CN)_5^{-3}$, Pd^{+2} , Pt^{+2} , Pt^{-4}
 Cu^+ , Ag^+ , Au^+ , Cd^{+2} , Hg^+ , Hg^{+2} , CH_3Hg^+
 BH_3 , $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3 , Tl^+ , $Tl(CH_3)_3$
 CH_2 , carbenes
 π -acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, etc.
 HO^+ , RO^+ , RS^+ , RSe^+ , Te^{+4} , RTe^+
 Br_2 , Br^+ , I_2 , I^+ , ICN , etc.
 O , Cl , Br , I , N , RO^+ , RO_2^+
 M^0 (metal atoms) and bulk metals

Table 7.7 Classification of hard and soft bases

Hard Bases

NH_3 , RNH_2 , N_2H_4
 H_2O , OH^- , O^{2-} , ROH , RO^- , R_2O
 CH_3COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^-
 F^- (Cl^-)

Borderline bases

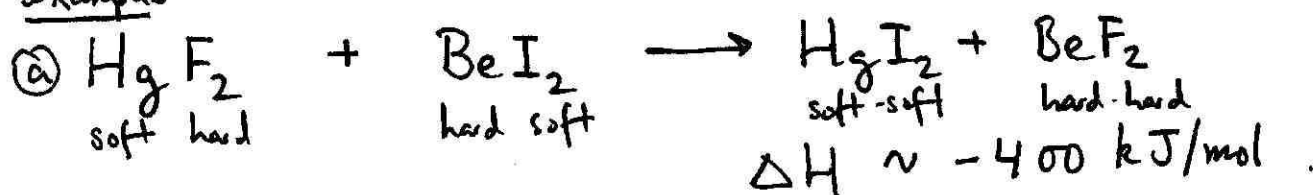
$C_6H_5NH_2$, C_6H_5N , N_3^- , N_2
 NO_2^- , SO_3^{2-}
 Br^-

Soft bases

H^-
 R^- , $C_2H_5^-$, $C_6H_5^-$, CN^- , RNC , CO
 SCN^- , R_3P , $(RO)_3P$, R_3As
 R_2S , RSH , RS^- , $S_2O_3^{2-}$
 I^-

The general rule is that a hard acid will associate to a hard base while a soft acid will associate with a soft base. This means it is better to make a good ionic bond & a good covalent bond rather than two bad ionic-covalent bonds.

examples



② benzene (soft) & water (hard) are not miscible.

③ The reaction of RNO_2 (hard) is fairly slow with hydride H^- (soft)

For next year of organic chemistry, whenever you deal with soft electrophiles & nucleophiles, the MO theory we taught in this course can be readily used. But when there are hard interactions \Rightarrow you may find thinking of an ionic picture will be more useful.

THE END OF THIS COURSE!
(I hope)

Ionic vs. MO model.

(Addenda for hard/soft lecture)

① When one looks over both organic & inorganic chemistry we can begin to see the dividing line for systems where we should consider the ionic model vs. the covalent model.

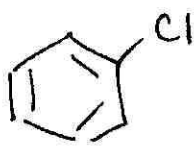
② In both organic and inorganic chemistry when the unit is $C \equiv N$, $C=O$, or $C=C$ we use the MO model. We've given two of examples of these in the course.

③ For halides such as F & Cl use the ionic model.

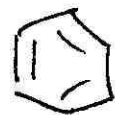
④ Thus $R-\overset{O}{\parallel}{C}-Cl$ is a better electrophile than



important. ⑤ Or, as a better example

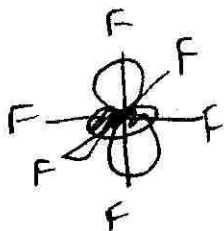


is slower at EAS than



(but as Cl is a π -donor it is o- & p-directly).

⑥ Or consider an electrostatic model for F & Cl in TF_6^{n+} or TCl_6^{k-}



is higher in energy electrostatically

than TCl_6 thus we would expect the spectrochemical order to be $F > Cl > Br > I$ which is correct

Ionic vs. MO model.

(Addressed for hard/soft letve)

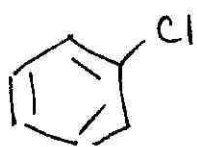
① When one looks over both organic & inorganic chemistry we can begin to see the dividing line for systems where we should consider the ionic model vs. the covalent model.

② In both organic and inorganic chemistry when the unit is $C \equiv N$, $C=O$, or $C=C$ we use the MO model. We've given two of examples of these in the course.

③ For halides such as F & Cl use the ionic model.

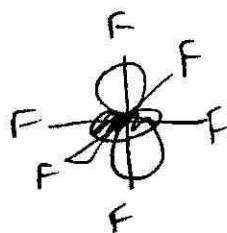
④ Thus $R-\overset{O}{\parallel}{C}-Cl$ is a better electrophile than $R-\overset{O}{\parallel}{C}-OH$, perhaps the picture $R-\overset{O}{\parallel}{C}^{\delta+}-Cl^{\delta-}$ is

important. ⑤ Or, as a better example



is slower at EAS than (but as Cl is a π -donor it is o- & p-directly).

⑥ Or consider an electrostatic model for F & Cl in TF_6^{n+} or TCl_6^{k-}



is higher in energy electrostatically than thus we would expect the spectrochemical order to be $F > Cl > Br > I$ which is correct

* If there is a mirror plane or C_2 then the MO's are either symmetric (S) or antisymmetric (A) with respect to this mirror plane.

To show (or at least indicate where this rule comes from) we prove the following.

Thm. Let $\vec{\psi}$ be an eigenvector of H with eigenvalue E_1 . Let $\vec{\psi}'$ be the only eigenvector (up to a constant) which has this eigenvalue.

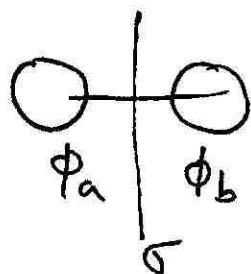
Then $\vec{\psi}'$ is either S or A with respect to a symmetry (σ or C_2) of the molecule.

Pf. If σ or C_2 are symmetries of the molecule, applying σ or C_2 leaves the molecule unchanged. It therefore leaves operators (or measurements) of the molecule unchanged

$$\therefore \sigma H = H \sigma.$$

Example

H_2



$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

$$H = \begin{matrix} & \phi_a & \phi_b \\ \phi_a & \alpha & \beta \\ \phi_b & \beta & \alpha \end{matrix}$$

$$\sigma \phi_a = \phi_b$$

$$\sigma \phi_b = \phi_a$$

So applying σ to H makes H into

$$\begin{matrix} & \phi_b & \phi_a \\ \phi_b & \alpha & \beta \\ \phi_a & \beta & \alpha \end{matrix}$$

Note H is unchanged. $\therefore \sigma$ has
no effect on H $\therefore \sigma H = H \sigma$

— So $H \psi_1 = E_1 \psi_1$

Now apply σ .

$$\sigma H \psi_1 = H(\sigma \psi_1)$$

$$\sigma E_1 \psi_1 = E_1(\sigma \psi_1)$$

Lecture 44. A last lecture?

① Writing this lecture, it's not completely clear to me that we will have the time for this lecture. My best guess is: this lecture will be ~~near~~ slope day.

What do I feel that I need tell you ~~in~~ the last days of classes?

Two things, both with an eye of preparing you for next year when most of you will go on to organic chemistry.

(a) A localized bonding picture for organic molecules

(b) The concepts of hard & soft.

② Organic chemists do not use a lot of MO theory when they think about their work. Instead, when they think about orbitals, they tend to use a localized picture. There are 3 general schemes of localized pictures which they use, which often go by the name sp^3 , sp^2 and sp .

So if $\vec{\psi}_1$ is an eigenvector ^{of \mathcal{H}} with eigenvalue E_1 , $\sigma \vec{\psi}_1$ is also an eigenvector of \mathcal{H} with eigenvalue E_1 . By our assumption 844.3

$$\sigma \vec{\psi}_1 = c \vec{\psi}_1$$

Where c is a constant.

σ does not change the length of $\vec{\psi}_1$.

$\therefore c = 1$ or -1

if $c = 1$ $\vec{\psi}_1$ is S

" $c = -1$ " " A