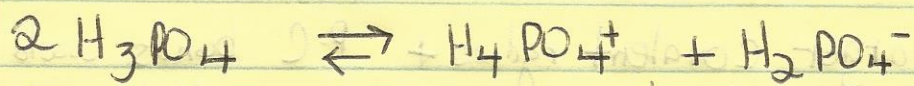
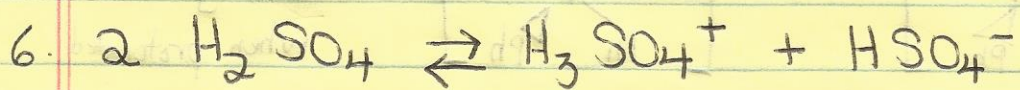


Ch. 6 HW

1.

	Acid	Base	Definition
a.	$AlBr_3$	$Br^-$	Lewis
b.	$HClO_4$	$CH_3CN$	Lewis, Brønsted-Lowry
c.	$Ni^{2+}$	$NH_3$	Lewis
d.	$ClF$	$NH_3$	Lewis
e.	$SO_2$	$ClO_3^-$	Lewis
f.	$HF$	$C_3H_7COOH$	Lewis, Brønsted-Lowry



form enough ions to allow conductance in the pure acids.

8. Basicity ranking

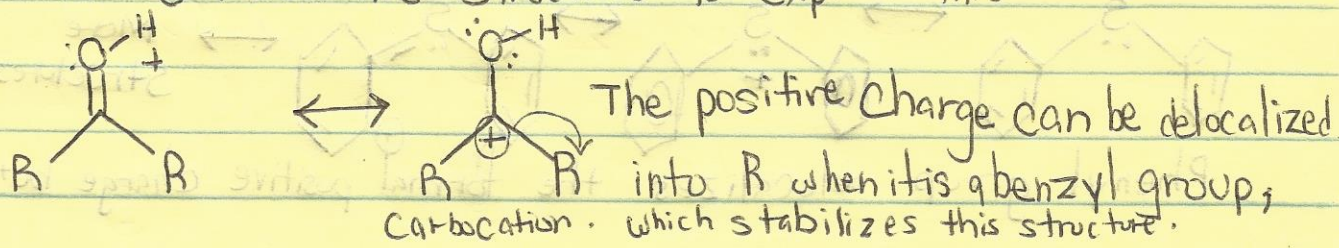
$CH_3COCH_3 < CH_3COCH_2CH_3 < PhCOPh$

proton affinities: 812.0 (kJ/mol) < 836.0 (kJ/mol) < 882.3 (kJ/mol)

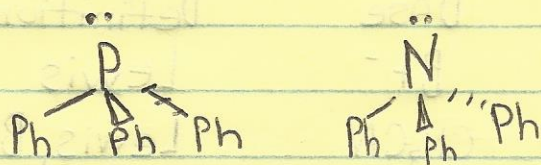
↑ proton affinity, ↑ basicity

The  $CH_2$  group in  $CH_3COCH_2CH_3$  donates  $e^-$  density to the carbocation, which stabilizes it.

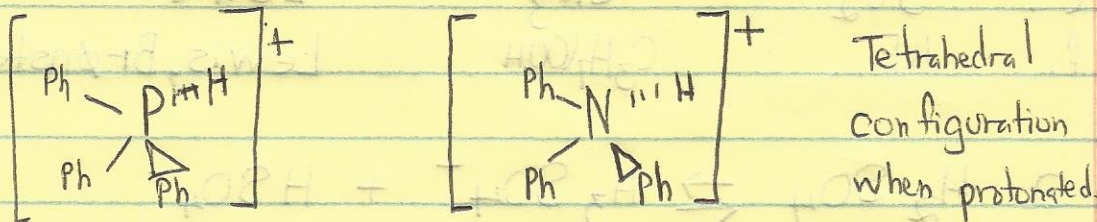
→ Look @ resonance structures to explain this.



### 9. Basicity ranking



$\chi_N > \chi_P$  and so you would expect the amine to be more basic. But sterics play a role here.

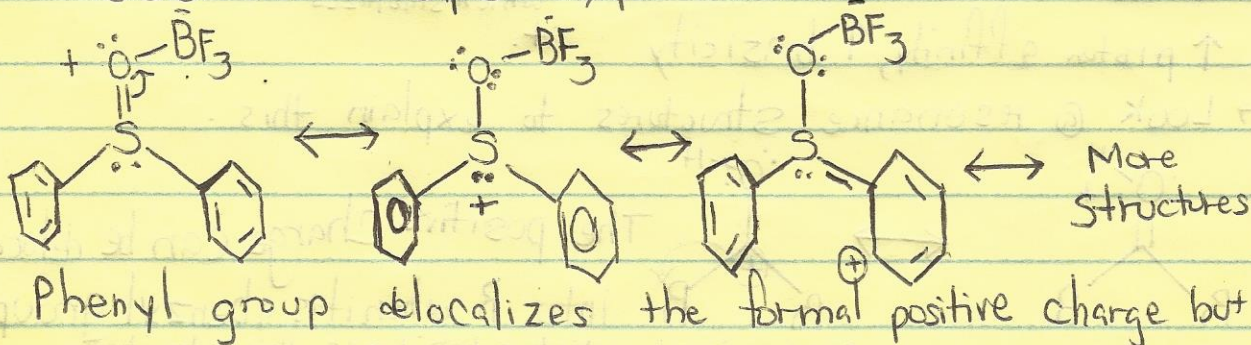


P has a larger covalent radius + P-C bonds would be longer than N-C. Therefore there would be less "back" strain in the Ph groups accommodating a tetrahedral geometry when the proton binds.

### 11. ↑ BF<sub>3</sub> affinity, ↑ Lewis basicity

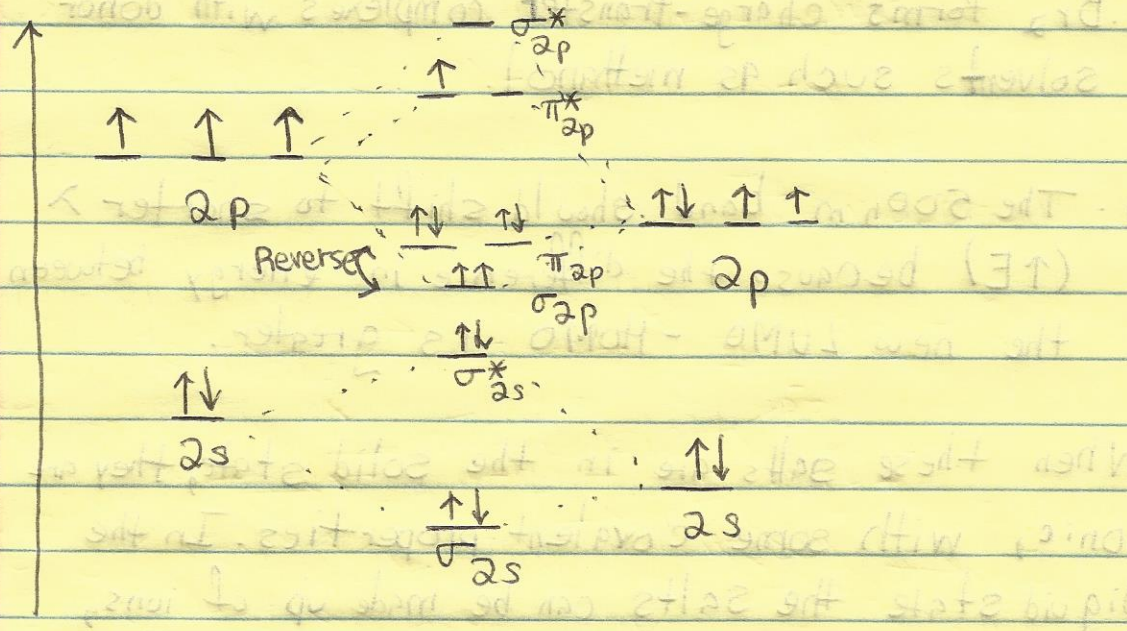
The electron-releasing ability of substituents in sulfoxides (R<sub>2</sub>SO) increases in the order of R: Ph, Me < nBu < cyclo-(CH<sub>2</sub>)

Resonance helps explain this.



the alkyl groups lower the formal positive charge.

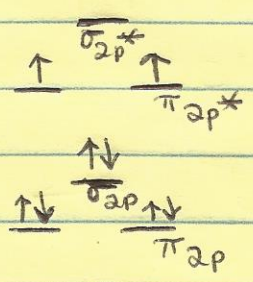
15. The N-O distance in the complex 2b is 129.6 pm, longer than the corresponding bond in free NO (115.1 pm).



LUMO is an antibonding orbital. Bond lengthening is expected since NO likely uses its  $\pi^*$  orbital (its LUMO) to accept  $e^-$  density from the phosphine. Population of an orbital that is antibonding with respect to the N-O bond will result in a longer bond distance.

21. See the MO diagram above

$\text{NO}^-$



(4)

Bonding with  $H^+$  depends on which end of the  $\pi^*$  orbital carries more  $e^-$  density. It is likely N because it is less  $\chi$ . This makes HNO more likely.

22. a.  $Br_2$  forms charge-transfer complexes with donor solvents such as methanol.

b. The  $500\text{ nm}$  band should shift to shorter  $\lambda$  ( $\uparrow E$ ) because the difference in energy between the new LUMO - HOMO is greater.

26. When these salts are in the solid state, they are ionic, with some covalent properties. In the liquid state the salts can be made up of ions, covalent molecules, or something in between. If the liquid is molecular, vaporization should be easier. If the liquid is mostly ionic, vaporization is more difficult. The most ionic liquids should be  $ZnF_2$  and  $CdF_2$  and the most molecular liquids should be  $HgF_2$  +  $HgCl_2$ . Hg, as the softest metal in the series, forms the more molecular compounds and zinc, as the hardest, forms the more ionic compounds.

27. a. pyridine +  $\text{BF}_3$

$$\Delta H = -(E_{\text{py}} E_{\text{BF}_3} + C_{\text{py}} C_{\text{BF}_3})$$

$$= -[(1.17)(9.88) + (6.40)(1.62)] = -21.9 \text{ kcal/mol}$$

$$\downarrow$$
$$-91.6 \text{ kJ/mol}$$

Roughly 13% less exothermic than the experimental value of  $-105 \text{ kJ/mol}$ .

pyridine +  $\text{B}(\text{CH}_3)_3$

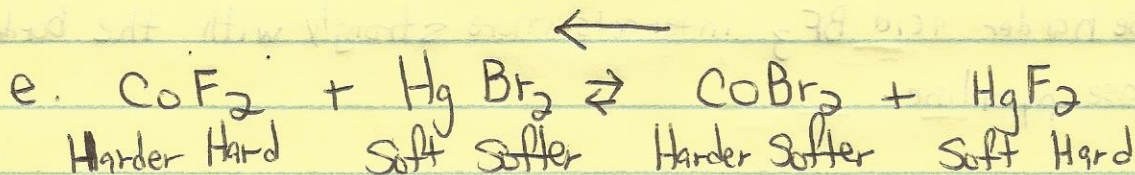
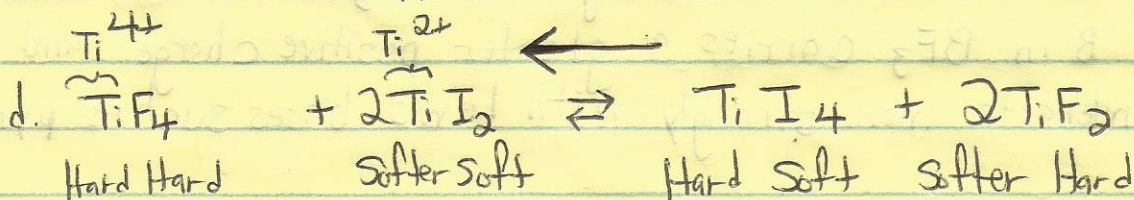
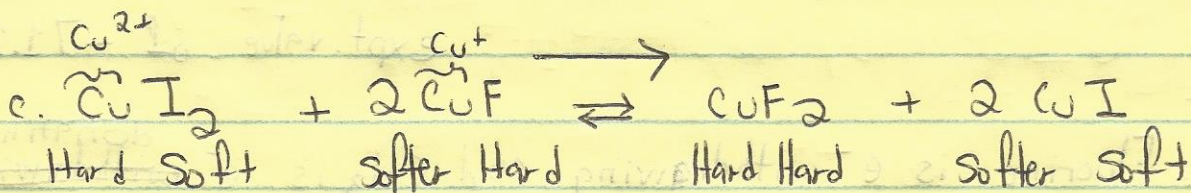
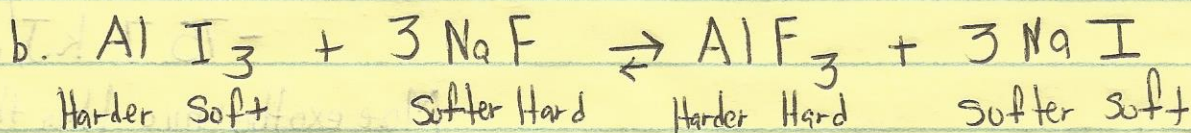
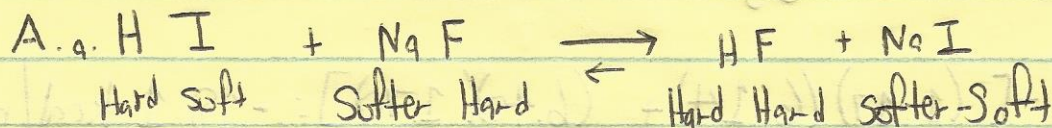
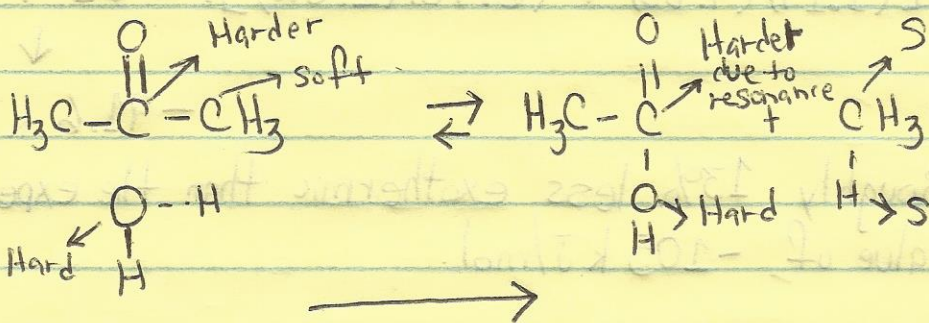
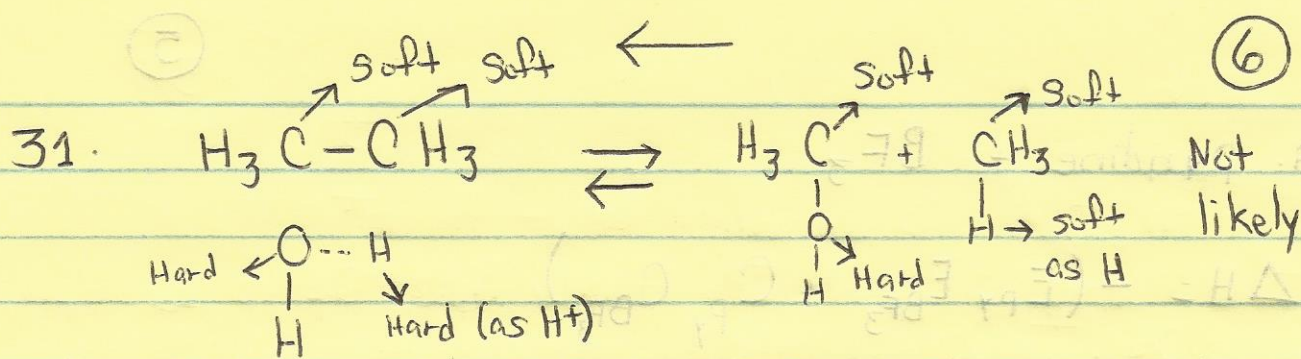
$$\Delta H = -[(1.17)(6.14) + (6.40)(1.70)] = -18.1 \text{ kcal/mol}$$

$$\downarrow$$
$$-75.7 \text{ kJ/mol}$$

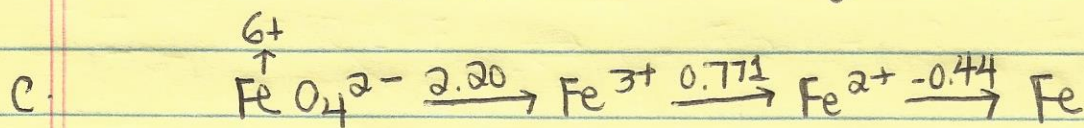
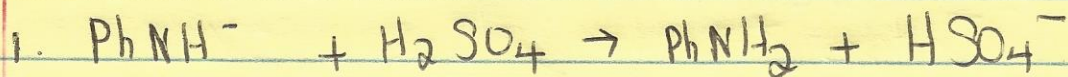
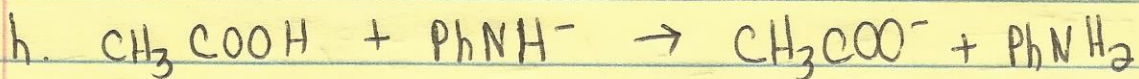
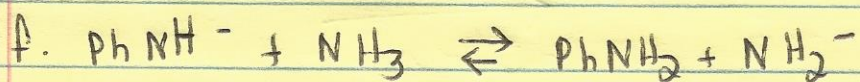
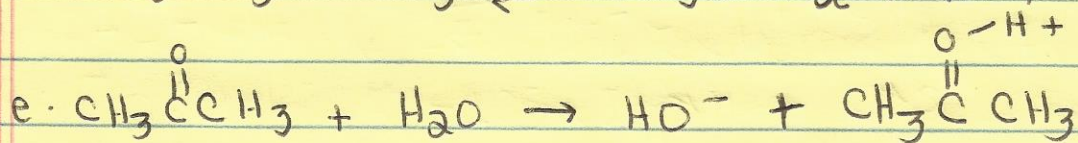
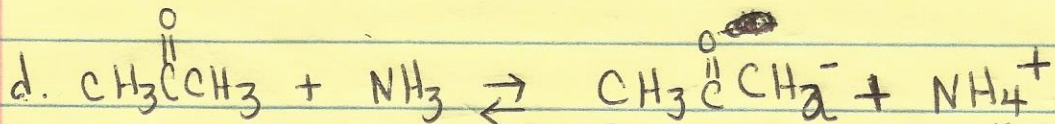
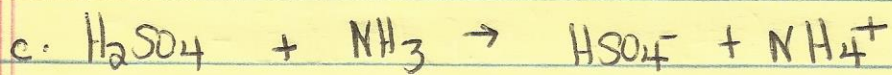
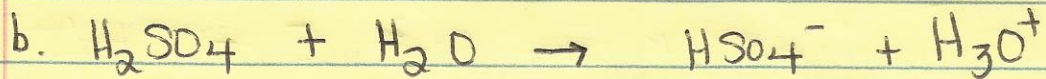
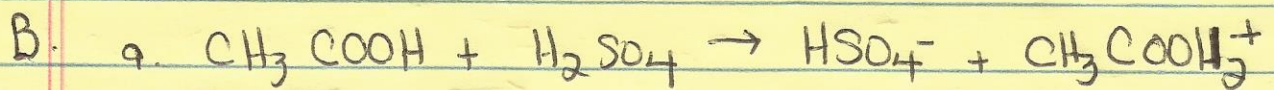
More exothermic than the expt. value of  $-71.1 \text{ kJ/mol}$

b. Fluorine is  $e^-$  withdrawing and  $\text{CH}_3$  is  $e^-$  donating.  
 $\therefore$  B in  $\text{BF}_3$  carries a greater positive charge and interacts more strongly with Lewis bases such as pyridine.

c. The harder acid  $\text{BF}_3$  interacts more strongly with the borderline base pyridine.



(7)



~~FeO<sub>4</sub><sup>2-</sup>~~

Spontaneous?

