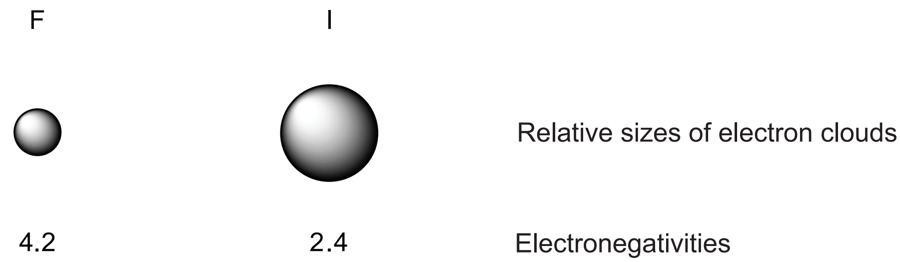
Activity 11B Hard Soft Acid Base Theory

Focus Question

Why are halogens good nucleophiles but very weak bases?

Model 1

Polarizability[1]



1. Which halogen in Model 1 has the largest electron cloud?

2. Which atom holds its electrons most tightly?

3. The polarizability of an atom or molecule is related to its size and electronegativity and can be defined qualitatively as the ability of the electron cloud to distort when exposed to an electric field; that is, an atom with a higher polarizability will have a larger induced dipole in an electric field. Which atom in Model 1 do you expect to have the higher polarizability? Explain your reasoning.

4. Polarizability is defined quantitatively as the magnitude of the dipole induced by one unit of field gradient. Iodine's polarizability is 4.7 and fluorine's is 0.557.[2] Does this information support your answer to question 3? If not, ask for help if you cannot determine the error in your reasoning.

MODEL 2

Hardness of Lewis Bases

One useful way of describing Lewis acids and bases is by a property called hardness. While hardness is technically a property of atoms, we find it useful to apply this concept to molecules as well. A hard atom or molecule in general is one with low polarizability and high electronegativity. A soft atom or molecule is the opposite.

Some Lewis bases:

a. $F^{\ominus}$, $HO^{\ominus}$ b. ethylene (C_2H_4), NH_3,

c. $(CH_3)_2S$, H_2O d. CH_3OH, $(CH_3)_3P$

5. Identify the pair of electrons in each Lewis base in Model 2 that would be donated in an acid-base reaction. You may find it helpful to draw out the Lewis structures.

6. In each pair of Lewis bases, circle the one that is harder. Explain your reasoning.

MODEL 3

Hardness of Lewis Acids

a. While the hardness of Lewis acids also depends on their polarizability and electronegativity, two other aspects of the acid must be taken into consideration. The actual (not formal) charge on the atom accepting the electrons. As the charge increases, the acid becomes harder.

b. For metal ions, the presence of valence lone pairs. Only metal ions that have at least a half-filled outer d shell are soft.

Some Lewis acids:

a. H^+, Hg^{2+} b. BF_3, BH_3,

c. Br_2, Na^+ d. Cr^{2+}, Ag^+

7. Explain what the difference is between the actual charge and the formal charge on an atom using hydronium ion as an example.

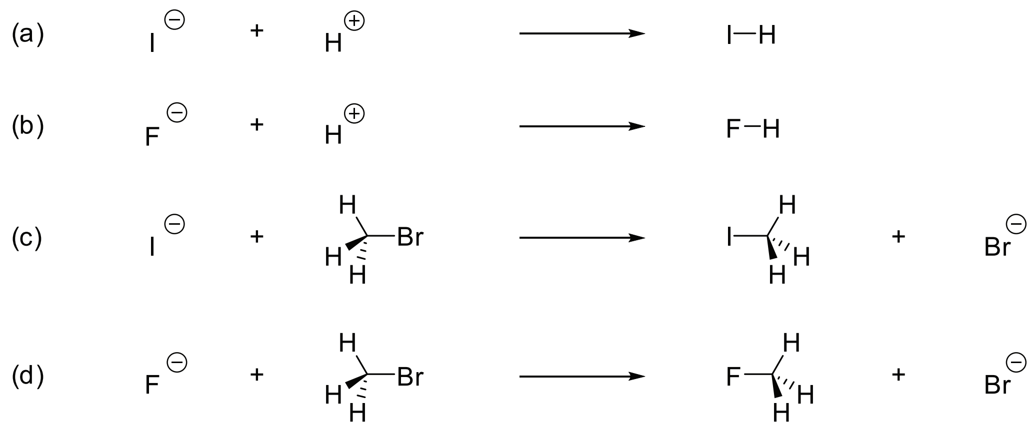
8. For those Lewis acids in Model 3 that contain more than one atom, identify the atom in each that would be accepting the pair of electrons in an acid-base reaction.

9. In each pair of Lewis acids, circle the one that is harder. Explain your reasoning.

10. Based on your knowledge of how electronegativity and polarizability affect the hardness of an atom or molecule, propose an explanation for (a) in Model 3. Then propose an explanation for (b).

Model 4

Hard Soft Acid Base Theory (HSAB)



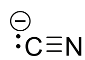
11. Draw curved arrows to show electron flow in the reactions above.
12. Circle the reactants that are acting as Lewis acids.
13. Put a box around the reactants that are acting as Lewis bases.
14. Predict which of the two different Lewis acids shown in Model 4 is harder.
15. Label each reaction in Model 4 as either an acid-base reaction or a substitution reaction
16. As discussed in the last activity, the nucleophilicity of halide ions does not parallel their basicity. For example, fluoride is a stronger base than iodide but a weaker nucleophile. Which acid base reaction above is more likely to occur? Which substitution reaction is most likely to occur?
17. What does your answer to question 16 suggest about the reactivity of a Lewis acid with a Lewis base with respect to hardness and softness?

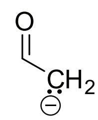
18. Hard Soft Acid Base theory (HSAB) says that “Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.”[3] Does this theory agree with your answer to question 16? If not, ask for help if you cannot determine the error in your reasoning.

Model 5

Ambident Nucleophiles

Ambident nucleophiles are molecules that have two different nucleophilic atoms. Cyanide ions and enolate ions are examples.





19. Circle the atoms in each molecule above that are nucleophilic. Explain your reasoning.

20. Of the two atoms that you just circled in cyanide, which is less electronegative?

21. Of the two atoms that you just circled in the enolate ion, which is more electronegative?

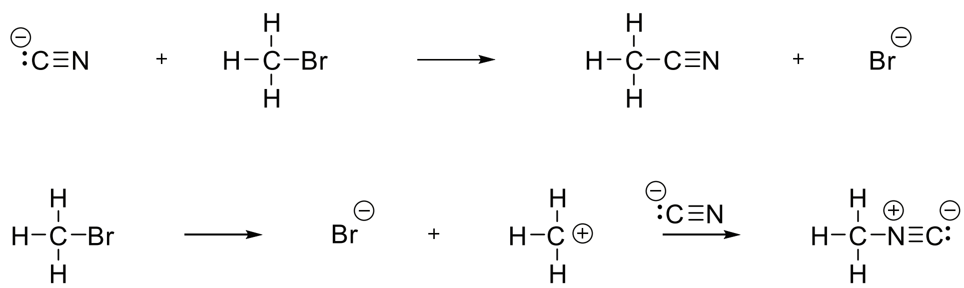
22. Of the two atoms that you just circled in cyanide, which is harder?

23. Of the two atoms that you just circled in the enolate ion, which is softer?

Model 6

Reactions of Ambident Nucleophiles

Ambident nucleophiles can react at either nucleophilic atom. Which atom this is depends on the particular reaction conditions.



24. Draw curved arrows to show electron flow in Model 6.

25. Label each reaction above with the name of its mechanism.

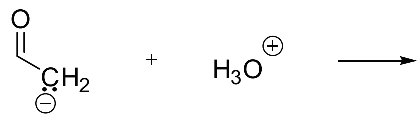
26. In each reaction, circle the Lewis acid that is reacting with the cyanide ion.

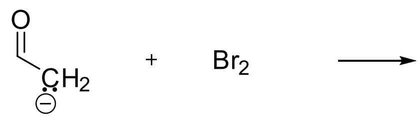
21. Which of the molecules that you circled in question 26 is hard? Which is soft? Explain your reasoning.

22. Explain why the carbon atom in cyanide ion acts as the nucleophile in the first reaction in Model 6 while the nitrogen atom acts as the nucleophile in the second reaction.

Exercises

1. Draw the products of the following reactions.





2. Predict the order of increasing reactivity of halide ions in an S_N2 reaction. Explain your reasoning.

3. Predict the order of increasing basicity of halide ions in water. Explain your reasoning.

Revisiting the Focus Question

Why are halogens good nucleophiles but very weak bases?

(Endnotes)

1 Electronegativities from Spencer, J. N.; Bodner, G. M; Rickard, L. H., *Chemistry Structure and Dynamics*, 3rd Edition; John Wiley and Sons: New York, 2006.

2 Anslyn, E. V.; Dougherty, D. A., *Modern Physical Organic Chemistry*; University Science Books: Sausalito, 2006.

3 Pearson, R. G. Hard and soft acids and bases, HSAB. *J. Chem. Ed.* **1968**, 45, 581-587.