**CHE2060: Understanding electrophiles & nucleophiles WS KEY**

**Identifying electrophiles and ranking their strength:**

Electrophiles are characterized by a lack of electrons, most often seen as a dipolar or full positive charge.
Full positive charge trumps dipolar positive charge.

**Identifying nucleophiles and ranking their strengths:**

All Nu: have a free pair of electrons and strong Nu:- have a full negative charge as the result of an ‘extra’ pair of unbounded electrons.
Four factors contribute to Nu: strength:

(1) **charge**: More negative charge indicates a stronger Nu:

(2) **electronegativity**: Nu: strength is inversely related to en values because electrons that are less tightly held are more available to be donated and make more dative bonds.
Within a row, electronegativity is a critical factor.

(3) **atomic size:** The larger the ion holding the pair of electrons to be donated the further those electrons are from the nucleus and thus they are more easily donated.
When comparing atoms in different rows, size is more important than electronegativity.

(4) **steric hindrance:** The less crowded the pair of electrons are the more easily they can form a new dative bond. So, the less bulky the molecule, particularly in proximity to the Nu:’s functional group, the better.
When comparing molecules with similar functional groups but different structures, molecular shape is a critical factor.

Solvent can be seen as a fifth factor, but that’s beyond the scope of this worksheet.

**NOTE:** Please draw **Lewis dot structures** of all molecules or ions whose structures are not shown and be sure to show all free electron pairs.

**Problems:**

**1.** Which would be the best nucleophile and why?

(a) CH3SH

**(b) CH3S-**

(c) CH3O-

(d) NH3

(e) H2O

Negative charge is a great indicator of nucleophilic strength, so (b) and (c) are the front-runners. While oxygen is more electronegative than sulfur, sulfur is larger than oxygen. So, sulfur (b) is the more stable anion because the larger sulfur atom is more comfortable carrying the negative charge, and because the free electron pair is held less tightly (and is therefore more available to form a dative bond) when it’s further from the nucleus.

**2.** Which is the strongest nucleophile, and why?

(a) CH3SH

(b) CH3SeH

(c) CH3OH

**(d) CH3TeH**

Here none of the choices carries a charge, so the factors affecting nucleophilic strength are electronegativity and ionic size. All options, S, Se, O, Te, are in the same column of the periodic table, so size is more of a factor than electronegativity. Te is the largest atom and ion, so it creates the largest and most stable anion because it is more comfortable carrying the negative charge, and because the free electron pair is held less tightly (and is therefore more available to form a dative bond) when it’s further from the nucleus.

**3.** Rank these in order of increasing nucleophilic strength.

(a) NH3

(b) H2O

(c) Cl-1

(d) F-1

**H2O < NH3 < F-1< Cl-1**

Again, negative charge determines the strongest nucleophiles. Fluorine is more electronegative than chlorine, so fluoride holds its ions more tightly as is a less effective nucleophile. When considering ammonia and water compare the relative electronegativity values of oxygen and nitrogen. Since nitrogen is less electronegative, ammonia is the stronger nucleophile.

**4.** Which of these is the ‘best’ nucleophile, and why? *How would you rank the rest?*

**(a) CN-1**

(b) CH3O-1

(c) OH-1

(d) (CH3)3CO-1

(e) (CH3)2CHO-1

CN-1 is the ‘best’ nucleophile.
All choices are negatively charged. All negatively charged atoms are N or O. N has a lower electronegativity value, making CN-1 the best choice. Of the others, O-based choices, the alkyl oxides (RO-1) are generally seen as slightly stronger bases and nucleophiles than OH-1 because of the presence of their alkyl groups. The alkyl group stabilizes the anion by delocalizing the negative charge of the oxygen over the neighboring carbon groups; a more stable anion is more likely to donate a free electron pair. Then bulkiness comes into play with the least bulky being the stronger nucleophile because bulkiness can prevent the free electron pair from having access to bonding: CH3O-1 > (CH3)2CHO-1 > (CH3)3CO-1 > OH-1.

**5.** When looking at a chemical equation or reaction mechanism involving a nucleophile, how can you tell when a nucleophile is acting as a base? (Remember that all bases are Nu: but not all Nu: are bases!)

**6.** Which is not an electrophile?

(a) CH3+1

(b) AlCl3

(c) H+1

**(d) (CH3)3N**

(e) all of the above
(CH3)3N is not an electrophile. The N has a free electron pair and is therefore a Nu:.

**7.** Which is not an electrophile?

(a) ZnCl2

(b) (CH3)3C+1

**(c) H3CCN**

(d) BF3

(e) all of the above

H3CCN is not an electrophile. The N has a free electron pair and is a nucleophile.

**8.** How can a carbonyl group act as either an electrophile or a nucleophile, or both?

The carbonyl group is polar: the oxygen has a dipolar negative charge and can act as a nucleophile, while the dipolar positive carbon can act as an electrophile. Carbonyls also have resonance structures, allowing them reactive ‘flexibility’.