

### Chapter 11 - Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

#### $S_N2$ Reaction Details - Nucleophile

The nucleophilicity of a reactant has a very loose correlation with its basicity, but they are not strictly correlated. For example, if you compare  $H_2O$  with  $HO^-$ , the latter will be more basic AND a more reactive nucleophile. However, if you compare  $HO^-$  and  $HS^-$ , the sulfide will be a much better nucleophile than the hydroxide. However, it is a weaker base. Thus, there is more to nucleophilicity than meets the eye. This has to do with how easily polarized the valence electrons are. If the atom is bigger and the valence electrons are further away from the nucleus, they are more easily polarized when approaching an electrophilic carbon. Thus, they can more easily form a bond. Electronegativity has a better correlation with nucleophilicity than does basicity. The more electronegative the atom, the less polarizable it is.

NUCLEOPHILE	$H_2O$	$NH_3$	$Cl^-$	$HO^-$	$CH_3O^-$	$I^-$	$CN^-$	$HS^-$
RELATIVE RATE FOR $S_N2$	1	700	1000	16,000	25,000	100,000	125,000	125,000

#### $S_N2$ Reaction Details - Leaving Group

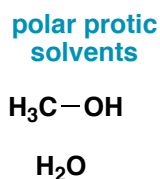
The leaving group has a big influence on the substitution reaction as well. The weaker the bond (longer bonds are weaker), the better a leaving group is. Also, the more stable the leaving group is after the bond has broken, the easier it can come off. Thus, more stable anions will be better leaving groups. The tosylate group ( $OTos$ ) is one of the best leaving groups.

LEAVING GROUP	$TosO^-$	$I^-$	$Br^-$	$Cl^-$	$F^-$	$HO^-$	$NH_2^-$
RELATIVE RATE FOR $S_N2$	60,000	30,000	10,000	200	1	<1	<1



#### $S_N2$ Reaction Details - Solvents

Solvents play a role in dissolving the reactants, stabilizing intermediates and can have positive or negative effects on a reaction. We will discuss the details next time. Here are some examples of common solvents. Note that 'protic' solvents can hydrogen bond with lone pairs.



#### polar aprotic solvents

