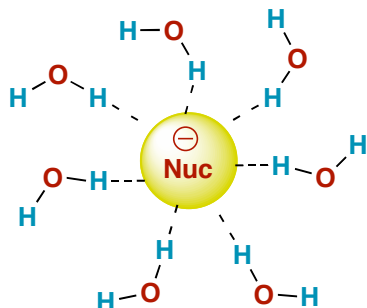


### Chapter 11 - Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

#### $S_N2$ Reaction Details - Solvents

Solvents play a role in dissolving the reactants, stabilizing intermediates and can have positive or negative effects on a reaction. In the  $S_N2$  reaction, the nucleophile strength is important. While solvents that are polar help any substitution reaction, protic solvents will retard the rate of  $S_N2$  reactions. This is because the acidic nature of the protons on water or alcohols will surround the nucleophile to stabilize it and render it less reactive. Polar aprotic solvents are best for  $S_N2$ .



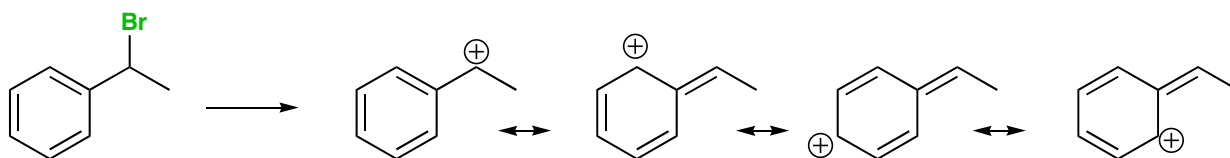
Polar protic solvents like water will surround a nucleophile making it less reactive. Thus, protic solvents retard the rate of  $S_N2$  reactions.

SOLVENT	CH <sub>3</sub> OH	H <sub>2</sub> O	DMSO	DMF	CH <sub>3</sub> CN	HMPA
RELATIVE RATE FOR $S_N2$	1	7	1300	2800	5000	200,000

#### $S_N1$ Reaction Details - Substrate

Since the nucleophile is not involved in the rate determining step of the  $S_N1$  reaction, the important feature here is the stability of the carbocation intermediate that is being formed. Tertiary substrates are best for this reaction. Secondary substrates are very slow, however if they are next to an alkene, resonance can greatly stabilize the carbocation and make  $S_N1$  more favorable.

SUBSTRATE				
	methyl	1°	2°	3°
RELATIVE RATE FOR $S_N1$	1	1	12	1,200,000



## S<sub>N</sub>1 Reaction Details - Nucleophile

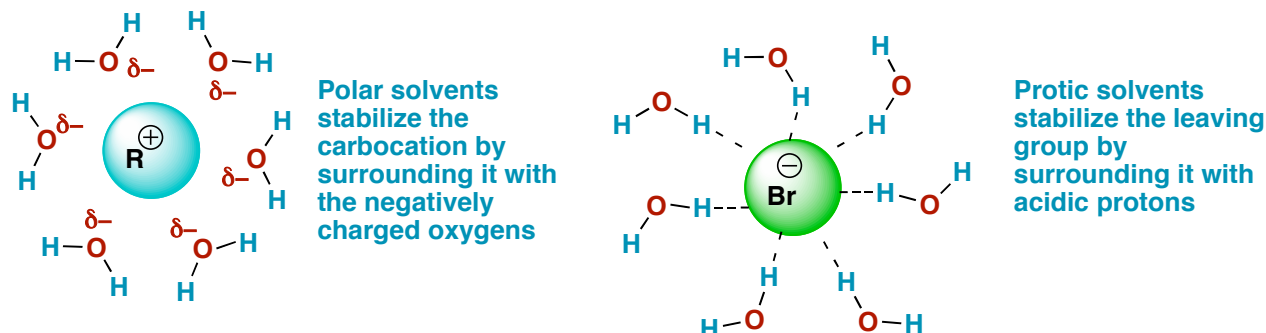
The nucleophile is not very important for a S<sub>N</sub>1 reaction. This is because it is not involved in the rate determining step. Even weak nucleophiles like neutral water will react with a carbocation when it's formed. The major concern is problems with competing elimination reactions when the nucleophile is too basic.

## S<sub>N</sub>1 Reaction Details - Leaving Group

The leaving group has a big influence on the substitution reaction for S<sub>N</sub>1 just as we saw with S<sub>N</sub>2 since the leaving group leaves in the rate determining step. 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 (<sup>-</sup>OTos) is one of the best leaving groups.

## S<sub>N</sub>1 Reaction Details - Solvents

What was bad for the nucleophile in S<sub>N</sub>2 reactions is great for the leaving group as it comes off. The protic solvents will stabilize the anion with its acidic protons. Also, the polar solvents will stabilize the carbocation when it's formed. Thus, polar protic solvents are best for aiding the rate determining step of the S<sub>N</sub>1 reaction.



## Stereochemistry of Substitution Reactions

S<sub>N</sub>2 reactions on chiral substrates will proceed with complete inversion of the stereochemistry. In a S<sub>N</sub>1 reaction, stereochemistry is lost when you form the planar (achiral) carbocation. The nucleophile may approach from either side with equal probability. Thus, racemic products are formed.

