

## 7.12: COMPARISON OF S<sub>N</sub>1 AND S<sub>N</sub>2 REACTIONS

### Learning Objective

- distinguish 1<sup>st</sup> or 2<sup>nd</sup> order substitution reactions

### PREDICTING S<sub>N</sub>1 VS. S<sub>N</sub>2 MECHANISMS

When considering whether a nucleophilic substitution is likely to occur via an S<sub>N</sub>1 or S<sub>N</sub>2 mechanism, we really need to consider three factors:

1) **The electrophile:** when the leaving group is attached to a methyl group or a primary carbon, an S<sub>N</sub>2 mechanism is favored (here the electrophile is unhindered by surrounded groups, and any carbocation intermediate would be high-energy and thus unlikely). When the leaving group is attached to a tertiary, allylic, or benzylic carbon, a carbocation intermediate will be relatively stable and thus an S<sub>N</sub>1 mechanism is favored. These patterns of reactivity of summarized below.

| Alkyl Halide Structure                     | Possible Substitution Reactions       |
|--|---------------------------------------|
| methyl and primary                         | S <sub>N</sub> 2 only                 |
| secondary                                  | S <sub>N</sub> 2 and S <sub>N</sub> 1 |
| tertiary                                   | S <sub>N</sub> 1 only                 |
| primary and secondary benzylic and allylic | S <sub>N</sub> 2 and S <sub>N</sub> 1 |
| tertiary benzylic and allylic              | S <sub>N</sub> 1 only                 |
| vinyl and aryl                             | NO reaction                           |

2) **The nucleophile:** powerful nucleophiles, especially those with negative charges, favor the S<sub>N</sub>2 mechanism. Weaker nucleophiles such as water or alcohols favor the S<sub>N</sub>1 mechanism.

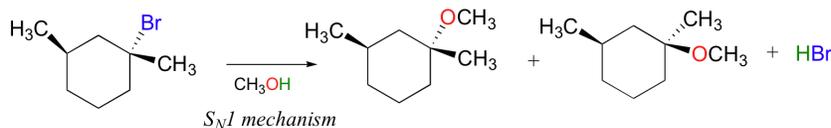
3) **The solvent:** Polar aprotic solvents favor the S<sub>N</sub>2 mechanism by enhancing the reactivity of the nucleophile. Polar protic solvents favor the S<sub>N</sub>1 mechanism by stabilizing the transition state and carbocation intermediate. S<sub>N</sub>1 reactions are called solvolysis reactions when the solvent is the nucleophile.

These patterns of reactivity are summarized in the table below.

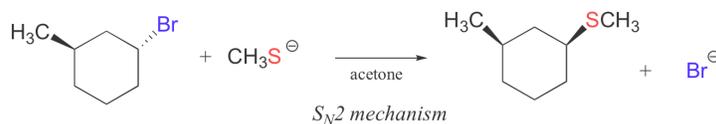
### COMPARISON BETWEEN S<sub>N</sub>2 AND S<sub>N</sub>1 REACTIONS

| Reaction Parameter     | S <sub>N</sub> 2                           | S <sub>N</sub> 1                           |
|------------------------|--|--|
| alkyl halide structure | methyl > primary > secondary >>>> tertiary | tertiary > secondary >>>> primary > methyl |
| nucleophile            | high concentration of a strong nucleophile | poor nucleophile (often the solvent)       |
| mechanism              | 1-step                                     | 2-stp                                      |
| rate limiting step     | bimolecular transition state               | carbocation formation                      |
| rate law               | rate = k[R-X][Nu]                          | rate = k[R-X]                              |
| stereochemistry        | inversion of configuration                 | mixed configuration                        |
| solvent                | polar aprotic                              | polar protic                               |

For example, the reaction below has a tertiary alkyl bromide as the electrophile, a weak nucleophile, and a polar protic solvent (we'll assume that methanol is the solvent). Thus we'd confidently predict an S<sub>N</sub>1 reaction mechanism. Because substitution occurs at a chiral carbon, we can also predict that the reaction will proceed with racemization.

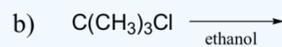


In the reaction below, on the other hand, the electrophile is a secondary alkyl bromide – with these, both S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms are possible, depending on the nucleophile and the solvent. In this example, the nucleophile (a thiolate anion) is strong, and a polar protic solvent is used – so the S<sub>N</sub>2 mechanism is heavily favored. The reaction is expected to proceed with inversion of configuration.



**Exercise**

1. Determine whether each substitution reaction shown below is likely to proceed by an  $S_N1$  or  $S_N2$  mechanism and explain your reasoning.


**Answer**

- a)  $S_N2$  b/c primary alkyl halide with a strong nucleophile in a polar aprotic solvent.
- b)  $S_N1$  b/c tertiary alkyl halide with a weak nucleophile that is also the solvent (solvolysis).
- c)  $S_N2$  b/c secondary alkyl halides favor this mechanism when reacted with a strong nucleophile (and weak base) in a polar aprotic solvent.

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