

7.12: COMPARISON OF SN1 AND SN2 REACTIONS

Learning Objective

- distinguish 1st or 2nd order substitution reactions

PREDICTING SN1 VS. SN2 MECHANISMS

When considering whether a nucleophilic substitution is likely to occur via an S_N1 or S_N2 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_N2 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_N1 mechanism is favored. These patterns of reactivity of summarized below.

Alkyl Halide Structure	Possible Substitution Reactions
methyl and primary	S _N 2 only
secondary	S _N 2 and S _N 1
tertiary	S _N 1 only
primary and secondary benzylic and allylic	S _N 2 and S _N 1
tertiary benzylic and allylic	S _N 1 only
vinyl and aryl	NO reaction

2) **The nucleophile:** powerful nucleophiles, especially those with negative charges, favor the S_N2 mechanism. Weaker nucleophiles such as water or alcohols favor the S_N1 mechanism.

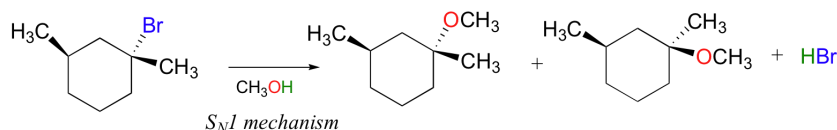
3) **The solvent:** Polar aprotic solvents favor the S_N2 mechanism by enhancing the reactivity of the nucleophile. Polar protic solvents favor the S_N1 mechanism by stabilizing the transition state and carbocation intermediate. S_N1 reactions are called solvolysis reactions when the solvent is the nucleophile.

These patterns of reactivity are summarized in the table below.

COMPARISON BETWEEN SN2 AND SN1 REACTIONS

Reaction Parameter	S _N 2	S _N 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_N1 reaction mechanism. Because substitution occurs at a chiral carbon, we can also predict that the reaction will proceed with racemization.

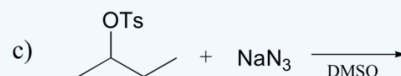
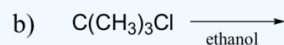


In the reaction below, on the other hand, the electrophile is a secondary alkyl bromide – with these, both S_N1 and S_N2 mechanisms are possible, depending on the nucleophile and the solvent. In this example, the nucleophile (a thiolate anion) is strong, and a polar protic solvent is used – so the S_N2 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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