

S_N1 and S_N2 Reactions

Consider the general reaction below:

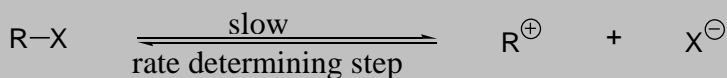


An alkyl halide reacts with an alcohol to form an ether and a strong acid.

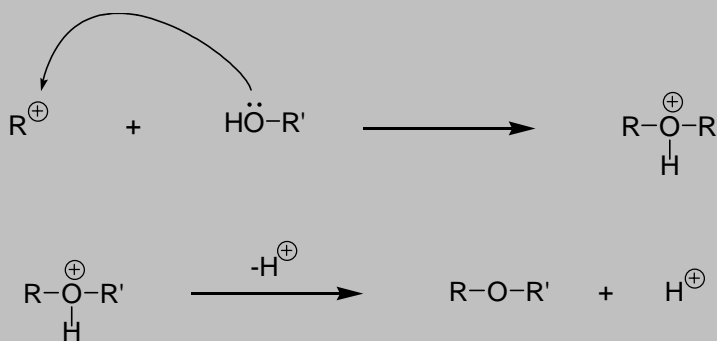
This reaction is described as a **NUCLEOPHILIC SUBSTITUTION** reaction because one nucleophile (⁻X) is substituted by another (⁻OR).

Although the reaction equation describes the reactants and the products formed, it says nothing of *how the reaction occurs*. The **mechanism** of a reaction describes how a reaction occurs. Nucleophilic substitution reactions can occur by one of two mechanisms; S_N1 or S_N2 pathways. The mechanism taken is dependent on the nature of the substrate R.

In the above reaction, If R is a group that stabilizes a carbocation, such as 'butyl, allyl, or benzyl, then the first step of the mechanism will be the dissociation of the carbon-halogen bond to form a carbocation. This is the slow, rate determining step.

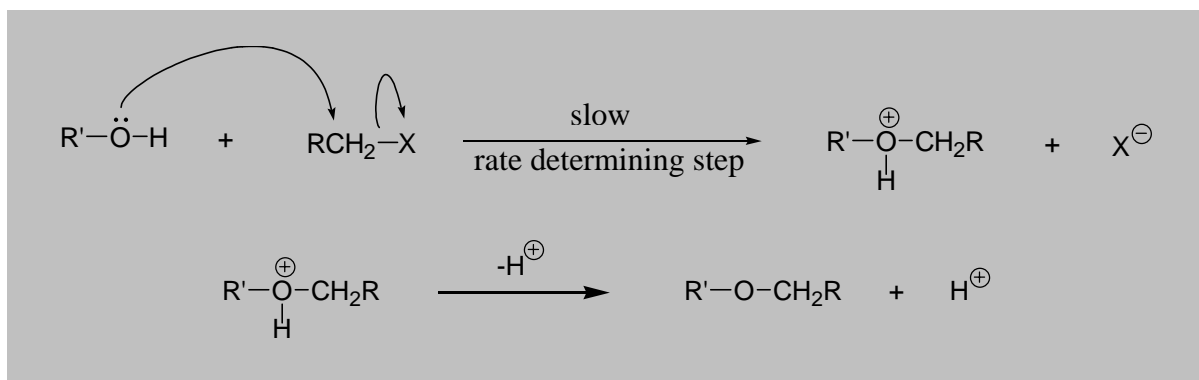


The carbocation then reacts rapidly with an alcohol to form an ether:



Because there is only *one reactant species* in the rate determining step, the alkyl halide, the reaction is first order and the mechanism is called S_N1 (substitution, nucleophilic, unimolecular). An S_N1 mechanism is followed when R is a tertiary alkyl group and sometimes followed when R is a secondary group.

When R is a primary alkyl group, the substitution occurs by an S_N2 mechanism. In this case, the rate determining step is attack at the primary carbon atom of the alkyl halide to directly form the ether:

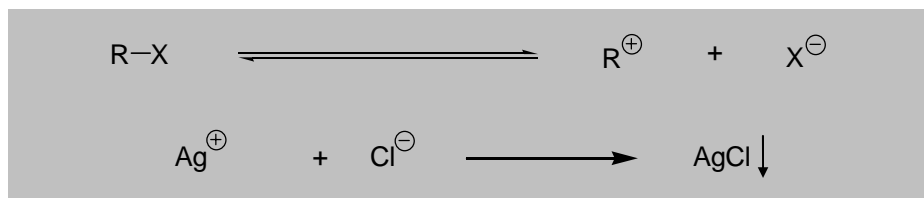


Because *two reactant species* are present in the rate determining step, the alkyl halide and the alcohol, the reaction is second order and the mechanism is called S_N2 (substitution, nucleophilic, bimolecular).

S_N1 Reactivity.

We are going to investigate the S_N1 mechanism by looking at the reaction of alkyl chlorides with ethanol in the presence of silver ions. The silver ions are used in the reaction for two reasons:

1. To drive the equilibrium of the rate determining step to the right by removing the Cl[−] ions from solution.
2. To give observable evidence that substitution has taken place. Silver chloride is insoluble in ethanol and will therefore precipitate from solution.



S_N2 Reactivity.

To study an S_N2 mechanism, we are going to look at the reaction between alkyl bromides and iodide ions. Iodide anions are good nucleophiles and in acetone solution react with alkyl bromides to form organic iodides:



Although this reaction is reversible, it can be driven forward by again taking advantage of a precipitated by-product. In anhydrous acetone, sodium iodide is soluble whereas sodium bromide is not. The speed of the reaction can be monitored by the formation of a sodium bromide precipitate. This mechanism involves a one-step, concerted, S_N2 displacement.

Warning: Silver nitrate is corrosive and light sensitive. Avoid all contact with exposed skin.

Warning: Allyl chloride and allyl bromide are both highly toxic. They are also suspected carcinogens. Handle only in the fumehood.

S_N1 Reactivity – Procedure:

Add 2 mL of 2% ethanolic silver nitrate in a test tube. Add 2 drops of the organic chloride to be tested, shake the test tube, and record the time required for a silver chloride precipitate to form. Test each of the following organic chlorides: 1-chlorobutane, 2-chlorobutane, 2-chloro-2-methylpropane, allyl chloride, and chlorobenzene. Use a sixth test tube containing only the silver nitrate solution as a comparison control.

S_N2 Reactivity – Procedure:

Add 2 mL of a 15% solution of sodium iodide in acetone to a test tube. Add 2 drops of the organic bromide to be tested, shake the test tube, and record the time required for a precipitate to form. Test each of the following organic bromides: 1-bromobutane, 2-bromobutane, 2-bromo-2-methylpropane, allyl bromide, and bromobenzene. Use a sixth test tube containing the sodium iodide-acetone solution as a comparison control.

S_N1 and S_N2 Reactions

Name: _____

Date: _____

Section: _____

Data:

Time for precipitate			
R group in RX	Structure of R group	Ag ⁺	I ⁻ in acetone
1-butyl			
2-butyl			
2-methyl-2-propyl			
allyl			
phenyl			

Questions:

1. Arrange the organic chlorides tested in order of decreasing reactivity toward Ag⁺:

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2. Explain the unusual position of allyl chloride in this series in view of the fact that it is a primary halide.

3. Give an explanation for the order of reactivity observed for the three saturated alkyl chlorides with Ag⁺.

4. Account for the low reactivity of chlorobenzene toward Ag^+ .
5. Arrange the organic bromides tested in order of decreasing reactivity toward I^- in acetone.
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6. Explain the position of allyl bromide in this series.
7. Explain the order of reactivity observed for the three saturated alkyl bromides with I^- .
8. Account for the reactivity of bromobenzene toward I^- .
9. Why must the acetone and the test tubes be scrupulously dry for the test with sodium iodide?