

7.4: SN1 Reaction Mechanism, Energy Diagram and Stereochemistry

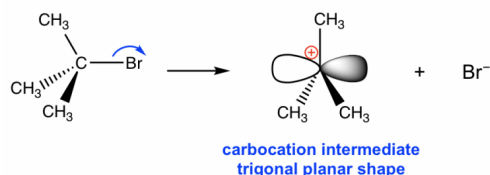
S_N1 Reaction Mechanism

The reaction between *tert*-butylbromide and water proceeds via the S_N1 mechanism. Unlike S_N2 that is a single-step reaction, S_N1 reaction involves multiple steps. Reaction: $(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$

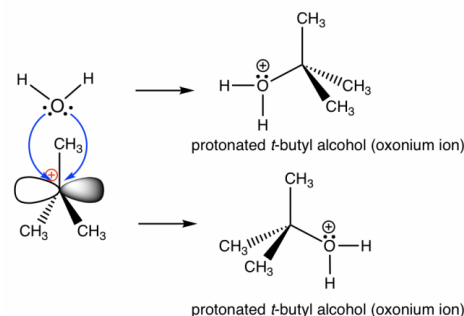


Mechanism:

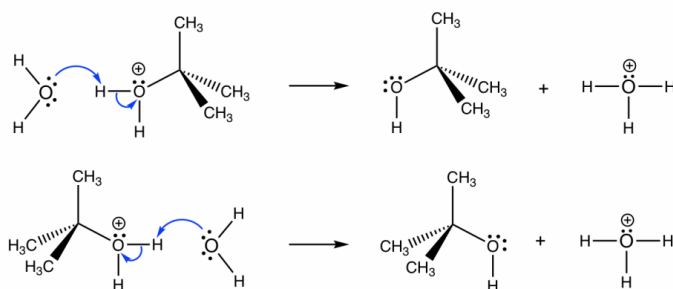
Step 1 Cleavage of C—Br bond **slowly** to form the carbocation intermediate. Step 1 is the **rate-determining step**.



Step 2 Rapid reaction between carbocation intermediate and nucleophile H₂O; H₂O attacks from both sides of the planar carbocation.



Step 3 Rapid deprotonation to produce neutral final product *t*-butyl alcohol (very fast step, and sometimes can be combined with step 2 together as one step).



In **step 1**, C—Br bond breaks and Br departs with the bonding electron pair to produce a tertiary carbocation and bromide anion Br[−]. This step only involves a highly endothermic bond-breaking process, and this is the slowest step in the whole mechanism. In multiple-step mechanism, the overall reaction rate is determined by the slowest step, such step is therefore called the **rate-determining step**. In S_N1 reaction, step 1 is the slowest step and therefore the rate-determining step. The rate-determining step only involves the alkyl halide substrate, that is why the overall rate law is in first order, because nucleophile does not participate in the rate-determining step.

The product of step 1, carbocation, will be the reactant of next step and is called the **intermediate** for S_N1 reaction. Intermediate is the unstable, highly-reactive species with very short lifetime. The carbocation intermediate is in trigonal planar shape, with the *empty* 2p orbital particular to the plane. The central carbon is sp² hybridized and has the incomplete octet, so carbocation is the highly reactive intermediate, that is also the electrophile.

Step 2 is the nucleophilic attack step, that the nucleophile H_2O use its lone pair to react with the carbocation intermediate, and produces the protonated *t*-butyl alcohol (oxonium ion). Because of the planar shape of carbocation intermediate, there is same possibility for the nucleophile to attack from either side of the plane, so possible products are generated with the same amounts. For this reaction, attacking from either side gives the same product (both are still shown for the purpose to illustrate the concept); however it gives different stereoisomers if the electrophilic carbon is the chirality center. In **step 3**, a water molecule acting as a Bronsted base to accept the proton from the oxonium ion, and the final neutral product *t*-butyl alcohol is produced. This deprotonation step is very fast, and sometimes can be combined with step 2 together as one step (i.e. step 3 may not be regarded as an individual step).

Energy diagram of $\text{S}_{\text{N}}1$ mechanism

Because $\text{S}_{\text{N}}1$ is a multiple-step reaction, so the diagram has multiple curves, with each step can be represented by one curve. Out of the three steps, the activation energy for step 1 is the highest, therefore step 1 is the slowest step, that is the rate-determining step.

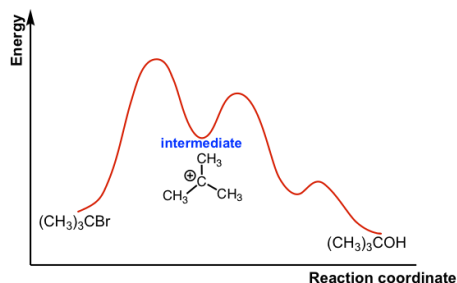


Figure 7.4a Energy diagram for $\text{S}_{\text{N}}1$ reaction between $(\text{CH}_3)_3\text{CBr}$ and H_2O

The connection between the first two curves represent the **carbocation intermediate**. Generally, intermediate is the product of one step of a reaction and the reactant for the next step. Intermediate is at a relatively lower energy level comparing to transition state (which is at the peak of a curve), but intermediate is also highly reactive and unstable.

The Effect of Substrate Structure on $\text{S}_{\text{N}}1$ Reaction Rate

Different substrates have different reaction rates towards $\text{S}_{\text{N}}1$ reaction, and the **relative reactivity of substrates towards $\text{S}_{\text{N}}1$ reaction** can be summarized as:

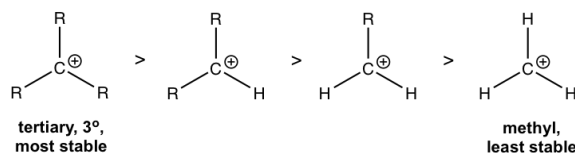
tertiary 3° > secondary 2° > primary 1° and methyl **too unreactive to undergo $\text{S}_{\text{N}}1$ reaction**

secondary 2 degree > primary 1 degree and methyl (too unreactive to undergo $\text{S}_{\text{N}}1$ reaction)" width="485" height="69"> Figure 7.4b Relative reactivity of substrates towards $\text{S}_{\text{N}}1$ reaction

Comparing this trend to that for $\text{S}_{\text{N}}2$ reaction, you probably realize that they are just opposite. Tertiary substrate is most reactive towards $\text{S}_{\text{N}}1$, but it does not undergo $\text{S}_{\text{N}}2$ at all; primary and methyl substrate are unreactive for $\text{S}_{\text{N}}1$, but they are the best substrates for $\text{S}_{\text{N}}2$. This comparison is very important and useful for us to choose the proper reaction condition for different substrate as we will see in next section. For now, we will need to understand the reasoning of the trend for $\text{S}_{\text{N}}1$.

This is because of the stability of carbocation intermediate. The mechanism shows that a carbocation is formed in the rate-determining step, so the more stable the carbocation, the more easily it is formed, the more it facilitates the rate-determining step and speed up the whole reaction. Therefore the more stable the carbocation intermediate is, the faster the rate of a $\text{S}_{\text{N}}1$ reaction.

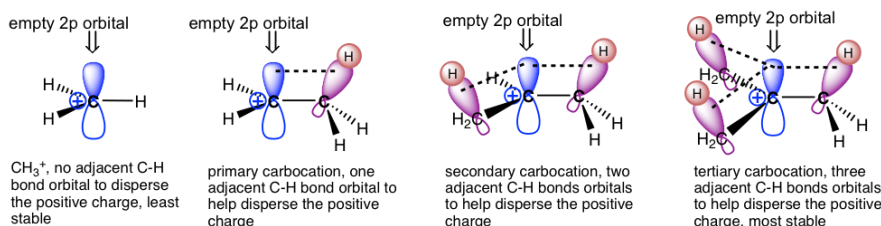
The relative stability of carbocation is given below, that the tertiary carbocations are the most stable and methyl carbocation is the least stable.



the relative stability of carbocations

Figure 7.4c The relative stability of carbocations

The relative stability of carbocations can be explained by the hyperconjugation effect. **Hyperconjugation** is the partial orbital overlap between filled bonding orbital to an adjacent unfilled (or half-filled) orbital. Carbocation is the electron-deficient species that has the incomplete octet and empty 2p orbital. If there is an alkyl group connected with carbocation, then there are C-C or C-H sigma bonds beside the carbocation carbon, so the filled orbitals of sigma bonds will be able to partially overlap with the empty 2p orbital, therefore sharing the electron density to carbocation and to get the carbocation stabilized. The more R group involved, the stronger hyperconjugation effect is. So tertiary (3°) carbocation is the most stable one. While there is no any R group in methyl carbocation, CH_3^+ , it is least stable.

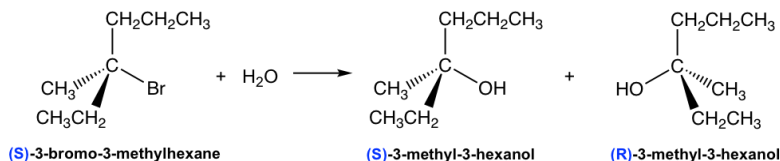


Hyperconjugation effect: electron delocalized from filled C-H orbitals to adjacent empty orbital, and helps to disperse and stabilize the positive charge

Figure 7.4d Hyperconjugation effect

Stereochemistry of $\text{S}_{\text{N}}1$ mechanism

The stereochemistry feature of the $\text{S}_{\text{N}}1$ reaction is very different to that of $\text{S}_{\text{N}}2$, and of course can be explained well with the $\text{S}_{\text{N}}1$ mechanism.



Starting with (S)-3-bromo-3-methylhexane reactant, the $\text{S}_{\text{N}}1$ reaction produces a 50:50 mixture of both R and S enantiomers of 3-methyl-3-hexanol, that is the **racemic mixture** product. This is because the carbocation formed in the first step of an $\text{S}_{\text{N}}1$ reaction has the trigonal planar shape, when it react with nucleophile, it may react from either the front side or the back side, and each side gives one enantiomer. There is equal possibility for reaction to occur from either side, so the two enantiomers are formed with the same amount, and the product is a racemic mixture.

A reaction that converts an optically active compound into a racemic form is said to proceed with **racemization**. For $\text{S}_{\text{N}}1$ reaction that start with (an optical active)one enantiomer as the reactant, and the chirality center is also the electrophilic carbon (i.e. the reaction occurs on the chirality center), it proceeds with racemization as shown above.

Exercises 7.3

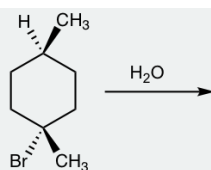
Show the detailed mechanism for above reaction of (S)-3-bromo-3-methylhexane and water.

Answers to Practice Questions Chapter 7

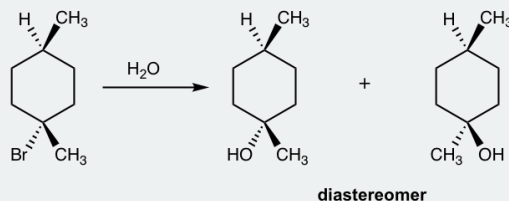
Please note that if the chirality center of the reactant is not the reaction center, or if there are more than one chirality center in the reactant, the $\text{S}_{\text{N}}1$ reaction does not produce the racemic mixture as example below.

Examples

Show product(s) of the following $\text{S}_{\text{N}}1$ reaction:



Solution:



Leaving Group Effect on S_N1

Same as for S_N2 reaction, a good leaving group is also required for S_N1 mechanism, and all the discussions we had before in [section 7.3](#) apply.

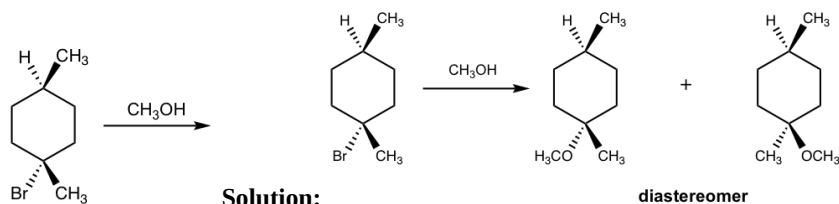
Nucleophile

Unlike a S_N2 reaction, the rate-determining step of S_N1 reaction does not include nucleophile, so theoretically the strength of nucleophile has no effect on S_N1 reaction. However, a strong nucleophile has high tendency to go with S_N2 reaction instead of S_N1 , so a weaker nucleophile is a better choice for S_N1 . For the examples we had so far, H_2O is the nucleophile.

In practice, neutral substances such as H_2O , ROH , $RCOOH$ are usually used as nucleophiles in S_N1 reaction. When these substances are applied in the reaction, they serve for another function as solvents. So they are used as *both* nucleophiles and solvents for S_N1 reaction, and such reaction is also called the solvolysis reaction. **Solvolysis reaction** is a nucleophilic substitution in which the nucleophile is a molecule of solvent as well. The term **solvolysis** comes from: *solvent*+*lysis*, that means cleavage by the solvent. A S_N1 reaction is usually a **solvolysis** reaction.

Examples

Show the structures of the products for the following solvolysis reaction.



Solution:

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