Objectives

After completing this section, you should be able to

1. discuss how the structure of the substrate affects the rate of a reaction occurring by the \( \text{SN}_1 \) mechanism.
2. arrange a given list of carbocations (including benzyl and allyl) in order of increasing or decreasing stability.
3. explain the high stability of the allyl and benzyl carbocations.
4. arrange a given series of compounds in order of increasing or decreasing reactivity in \( \text{SN}_1 \) reactions, and discuss this order in terms of the Hammond postulate.
5. discuss how the nature of the leaving group affects the rate of an \( \text{SN}_1 \) reaction, and in particular, explain why \( \text{SN}_1 \) reactions involving alcohols are carried out under acidic conditions.
6. explain why the nature of the nucleophile does not affect the rate of an \( \text{SN}_1 \) reaction.
7. discuss the role played by the solvent in an \( \text{SN}_1 \) reaction, and hence determine whether a given solvent will promote reaction by this mechanism.
8. compare the roles played by the solvent in \( \text{SN}_1 \) and in \( \text{SN}_2 \) reactions.
9. determine which of two \( \text{SN}_1 \) reactions will occur faster, by taking into account factors such as the structure of the substrate and the polarity of the solvent.
10. determine whether a given reaction is most likely to occur by an \( \text{SN}_1 \) or \( \text{SN}_2 \) mechanism, based on factors such as the structure of the substrate, the solvent used, etc.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- benzylic
- dielectric constant
- polarity

\( \text{SN}_1 \) Mechanism

The first order kinetics of \( \text{SN}_1 \) reactions suggests a two-step mechanism in which the rate-determining step consists of the ionization of the alkyl halide, as shown in the diagram below. In this mechanism, a carbocation is formed as a high-energy intermediate, and this species bonds immediately to nearby nucleophiles. If the nucleophile is a neutral molecule, the initial product is an "onium" cation, as drawn above for t-butyl chloride, and presumed in the energy diagram. In evaluating this mechanism, we may infer several outcomes from its function.
The only reactant that is undergoing change in the first (rate-determining) step is the alkyl halide, so we expect such reactions would be unimolecular and follow a first-order rate equation. Hence the name $S_{N}1$ is applied to this mechanism.

1. Since nucleophiles only participate in the fast second step, their relative molar concentrations rather than their nucleophilicities should be the primary product-determining factor. If a nucleophilic solvent such as water is used, its high concentration will assure that alcohols are the major product. Recombination of the halide anion with the carbocation intermediate simply reforms the starting compound. Note that $S_{N}1$ reactions in which the nucleophile is also the solvent are commonly called solvolysis reactions. The hydrolysis of $t$-butyl chloride is an example.

2. The activation energy of the rate-determining first step will be proportional to the stability of the carbocation intermediate (more stable carbocations will reduce activation energy). The stability of carbocations was discussed earlier, and a qualitative relationship is given below.

<table>
<thead>
<tr>
<th>Carbocation</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3^{(+)}$</td>
<td>$&lt; \text{CH}_3\text{CH}_2^{(+)}$</td>
</tr>
</tbody>
</table>
Consequently, we expect that 3º-alkyl halides will be more reactive than their 2º and 1º-counterparts in reactions that follow an S$_N$1 mechanism. This is opposite to the reactivity order observed for the S$_N$2 mechanism. Allylic and benzylic halides are exceptionally reactive by either mechanism.

3. In order to facilitate the charge separation of an ionization reaction, as required by the first step, a good ionizing solvent will be needed. Two solvent characteristics will be particularly important in this respect. The first is the ability of solvent molecules to orient themselves between ions so as to attenuate the electrostatic force one ion exerts on the other. This characteristic is related to the dielectric constant, ε, of the solvent. Solvents having high dielectric constants, such as water (ε=81), formic acid (ε=58), dimethyl sulfoxide (ε=45) & acetonitrile (ε=39) are generally considered better ionizing solvents than are some common organic solvents such as ethanol (ε=25), acetone (ε=21), methylene chloride (ε=9) & ether (ε=4). The second factor is solvation, which refers to the solvent's ability to stabilize ions by encasing them in a sheath of weakly bonded solvent molecules. Anions are solvated by hydrogen-bonding solvents, as noted earlier. Cations are often best solvated by nucleophilic sites on a solvent molecule (e.g. oxygen & nitrogen atoms), but in the case of carbocations these nucleophiles may form strong covalent bonds to carbon, thus converting the intermediate to a substitution product. This is what happens in the hydrolysis reactions described above.

4. The stereospecificity of these reactions may vary. The positively-charged carbon atom of a carbocation has a trigonal planar (flat) configuration (it prefers to be sp$^2$ hybridized), and can bond to a nucleophile equally well from either face. If the intermediate from a chiral alkyl halide survives long enough to encounter a random environment, the products are expected to be racemic (a 50:50 mixture of enantiomers). On the other hand, if the departing halide anion temporarily blocks the front side, or if a nucleophile is oriented selectively at one or the other face, then the substitution might occur with predominant inversion or even retention of configuration.

5. Just as with S$_N$2 reactions, the nucleophile, solvent and leaving group also affect S$_N$1 (Unimolecular Nucleophilic Substitution) reactions. Polar protic solvents have a hydrogen atom attached to an electronegative atom so the hydrogen is highly polarized. Polar aprotic solvents have a dipole moment, but their hydrogen is not highly polarized. Polar aprotic solvents are not used in S$_N$1 reactions because some of them can react with the carbocation intermediate and give you an unwanted product. Rather, polar protic solvents are preferred.

The strength of the nucleophile does not affect the reaction rate of S$_N$1 because, as stated above, the nucleophile is not involved in the rate-determining step. However, if you have more than one nucleophile competing to bond to the carbocation, the strengths and concentrations of those nucleophiles affects the distribution of products that you will get. For example, if you have (CH$_3$)$_3$CCl reacting in water and formic acid where the water and formic acid are competing nucleophiles, you will get two different products: (CH$_3$)$_3$COH and (CH$_3$)$_3$COCOH. The relative yields of these products depend on the concentrations and relative reactivities of the nucleophiles.

**Solvent Effects on the S$_N$1 Reaction**

Since the hydrogen atom in a polar protic solvent is highly positively charged, it can interact with the anionic nucleophile which would negatively affect an S$_N$2, but it does not affect an S$_N$1 reaction because the nucleophile is not a part of the rate-determining step. Polar protic solvents actually speed up the rate of the unimolecular substitution reaction because the large dipole moment of the solvent helps to stabilize the transition state. The highly positive and highly negative parts interact with the substrate to lower the energy of the transition state.
Since the carbocation is unstable, anything that can stabilize this even a little will speed up the reaction.

Sometimes in an \( \text{S}_\text{N}1 \) reaction the solvent acts as the nucleophile. This is called a solvolysis reaction. The \( \text{S}_\text{N}1 \) reaction of allyl bromide in methanol is an example of what we would call **methanolysis**, while if water is the solvent the reaction would be called **hydrolysis**:

\[
\text{\begin{align*}
\text{Br} & \quad \text{CH}_2\text{OH} & \quad \text{OCH}_3 & + \text{HBr} & \quad \text{methanolysis} \\
\text{Br} & \quad \text{H}_2\text{O} & \quad \text{OH} & + \text{HBr} & \quad \text{hydrolysis}
\end{align*}}
\]

The polarity and the ability of the solvent to stabilize the intermediate carbocation is very important as shown by the relative rate data for the solvolysis (see table below). The dielectric constant of a solvent roughly provides a measure of the solvent's polarity. A dielectric constant below 15 is usually considered non-polar. Basically, the dielectric constant can be thought of as the solvent's ability to reduce the internal charge of the solvent. So for our purposes, the higher the dielectric constant the more polar the substance and in the case of \( \text{S}_\text{N}1 \) reactions, the faster the rate.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CO}_2\text{H} )</td>
<td>( 6 )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>( 33 )</td>
<td>( 4 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>( 78 )</td>
<td>( 150,000 )</td>
</tr>
</tbody>
</table>

Below is the same reaction conducted in two different solvents and the relative rate that corresponds with it.

\[
\begin{align*}
\text{Relative Rate: 150,000} \\
\text{Relative Rate: 4}
\end{align*}
\]

The figure below shows the mechanism of an \( \text{S}_\text{N}1 \) reaction of an alkyl halide with water. Since water is also the solvent, this is an example of a solvolysis reaction.

Examples of polar protic solvents are: acetic acid, isopropanol, ethanol, methanol, formic acid, water, etc.

**Effects of Nucleophile**

The strength of the *nucleophile* does not affect the reaction rate of \( \text{S}_\text{N}1 \) because, as stated above, the nucleophile is not
involved in the rate-determining step. However, if you have more than one nucleophile competing to bond to the carbocation, the strengths and concentrations of those nucleophiles affects the distribution of products that you will get. For example, if you have (CH$_3$)$_3$CCl reacting in water and formic acid where the water and formic acid are competing nucleophiles, you will get two different products: (CH$_3$)$_3$COH and (CH$_3$)$_3$COCOH. The relative yields of these products depend on the concentrations and relative reactivities of the nucleophiles.

Effects of Leaving Group

An S$_N$1 reaction speeds up with a good leaving group. This is because the leaving group is involved in the rate-determining step. A good leaving group wants to leave so it breaks the C-Leaving Group bond faster. Once the bond breaks, the carbocation is formed and the faster the carbocation is formed, the faster the nucleophile can come in and the faster the reaction will be completed.

A good leaving group is a weak base because weak bases can hold the charge. They're happy to leave with both electrons and in order for the leaving group to leave, it needs to be able to accept electrons. Strong bases, on the other hand, donate electrons which is why they can't be good leaving groups. As you go from left to right on the periodic table, electron donating ability decreases and thus ability to be a good leaving group increases. Halides are an example of a good leaving group whose leaving-group ability increases as you go down the column.

The two reactions below is the same reaction done with two different leaving groups. One is significantly faster than the other. This is because the better leaving group leaves faster and thus the reaction can proceed faster.
Other examples of good leaving groups are sulfur derivatives such as methyl sulfate ion and other sulfonate ions (See Figure below)

Predicting $S_N1$ vs. $S_N2$ mechanisms; competition between nucleophilic substitution and elimination reactions

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.

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 carbocation intermediate. $S_N1$ reactions are frequently solvolysis reactions.

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 aprotic solvent is used – so the $S_N2$ mechanism is heavily favored. The reaction is expected to proceed with inversion of configuration.

**Exercise 8.15**: Determine whether each substitution reaction shown below is likely to proceed by an $S_N1$ or $S_N2$ mechanism.

a) $\text{Br} + \text{NaOCH}_3 \xrightarrow{\text{acetone}}$

b) $\text{C(CH}_3)_3\text{Cl} \xrightarrow{\text{ethanol}}$

c) $\text{OTs} + \text{NaN}_3 \xrightarrow{\text{DMSO}}$
Exercise \(\PageIndex{1}\))

1. Put the following leaving groups in order of decreasing leaving group ability

\[
\text{H} \quad \text{O} \quad \text{Br} \quad \text{CH}_3
\]

2. Which solvent would an SN1 reaction occur faster in? \(\text{H}_2\text{O}\) or \(\text{CH}_3\text{CN}\)

3. What kind of conditions disfavor \(\text{SN}_1\) reactions?

4. What are the products of the following reaction and does it proceed via \(\text{SN}_1\) or \(\text{SN}_2\)?

5. How could you change the reactants in the problem 4 to favor the other substitution reaction?

6. Indicate the expected product and list why it occurs through \(\text{SN}_1\) instead of \(\text{SN}_2\)?

Answers

2. An \(\text{SN}_1\) reaction would occur faster in \(\text{H}_2\text{O}\) because it's polar protic and would stabilize the carbocation and \(\text{CH}_3\text{CN}\) is polar aprotic.

3. Polar aprotic solvents, a weak leaving group and primary substrates disfavor \(\text{SN}_1\) reactions.
Reaction proceeds via SN1 because a tertiary carbocation was formed, the solvent is polar protic and Br- is a good leaving group.

5. You could change the solvent to something polar aprotic like CH3CN or DMSO and you could use a better base for a nucleophile such as NH2- or OH-.

6. This reaction occurs via SN1 because Cl- is a good leaving group and the solvent is polar protic. This is an example of a solvolysis reaction because the nucleophile is also the solvent.

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**Exercises**

**Questions**

**Q11.5.1**

Rank the following by increasing reactivity in an SN1 reaction.

A) \[
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\]

B) \[
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\]

C) \[
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\]

D) \[
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\]

**Q11.5.2**
3-bromo-1-pentene and 1-bromo-2-pentene undergo $S_N1$ reaction at almost the same rate, but one is a secondary halide while the other is a primary halide. Explain why this is.

**Q11.5.3**

Label the following reactions as most likely occurring by an $S_N1$ or $S_N2$ mechanism. Suggest why.

![Reaction A](image1.png)\[A\]
\[\text{OH} \xrightarrow{\text{HBr, CH}_2\text{CH}_2\text{OH}} \text{Br}^{-}\]

![Reaction B](image2.png)\[B\]
\[\text{Br} \xrightarrow{\text{Na}^+, \text{SCH}_3, \text{CH}_3\text{CN}} \text{SCH}_3\]

**Solutions**

**S11.5.1**

Consider the stability of the intermediate, the carbocation.

A $<$ D $<$ B $<$ C (most reactive)

**S11.5.2**

They have the same intermediates when you look at the resonance forms.

**S11.5.3**

A – $S_N1$ *poor leaving group, protic solvent, secondary cation intermediate*

B – $S_N2$ *good leaving group, polar solvent, primary position.*
Contributors

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Ashiv Sharma
- Layne Morsch (University of Illinois Springfield)