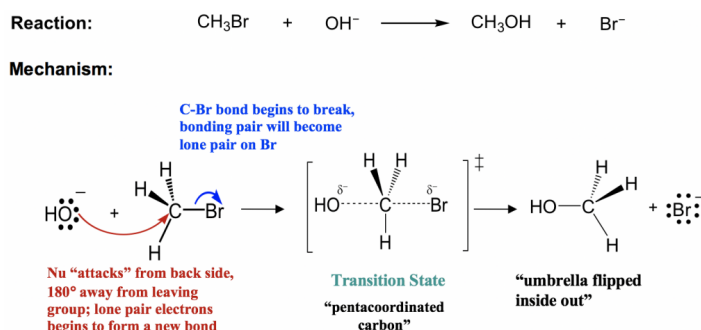


7.2: S_N2 Reaction Mechanism, Energy Diagram and Stereochemistry

S_N2 Reaction Mechanism

Let's still take the reaction between CH₃Br and OH⁻ as the example for S_N2 mechanism.



S_N2 mechanism involves two electron pair transfers that occur at the same time, nucleophile attacking (red arrow) and leave group leaving (blue arrow). The nucleophile OH⁻ approaches the electrophilic carbon from the back side, the side that is opposite to the direction that leaving group Br leaves. With the nucleophile OH⁻ getting closer, the Br start to leave as well. The new C—OH bond formation and the old C—Br bond breaking occur *at the same time*. In a very short transient moment, the carbon atom is *partially* connected with *both* OH and Br, that gives a highest energy level state of the whole process called **transition state**. In the transition state of S_N2 reaction, there are *five* groups around the carbon and the carbon can be called "pentacoordinated". As the OH⁻ continues to get closer to the carbon, the Br moves further away from it with the bonding electron pair. Eventually, the new bond is completely formed and the old bond is completely broken that gives the product CH₃OH.

In the mechanism, the reaction proceeds in a single step that involves both nucleophile and the substrate, so increasing the concentration of either of them makes the possibility of collision increase, that explains the **second-order** kinetics of S_N2 reaction. With both nucleophile attacking and leaving group leaving happen at the same time, S_N2 is also said to be a **concerted** mechanism, concerted means simultaneous.

Notes for drawing S_N2 mechanism:

- The **two** arrows must be shown when drawing the S_N2 mechanism. Both have to be shown with the proper direction: nucleophile attack from the direction that is **opposite** to the leaving group leaves, *i.e.*, backside attack.
- The transition state is optional (depends on the requirement of the question). However it is important to understand that the reaction process goes through the transition state before producing the products.
- Please pay attention that for the product, the positions of the three hydrogens around carbon are all pushed to the other side, and the overall configuration of the carbon get *inverted*, like an umbrella flipped inside out in a windstorm. It seems does not really matter for product (CH₃OH) in this reaction, however it does make a difference if the carbon is a chirality center.

Energy Diagram of S_N2 Mechanism

The energy changes for the above reaction can be represented in the energy diagram shown in **Fig. 7.1**. S_N2 is a single-step reaction, so the diagram has only one curve. The products CH₃OH and Br⁻ are in lower energy than the reactants CH₃Br and OH⁻, indicates that the overall reaction is **exothermic** and the products are more stable.

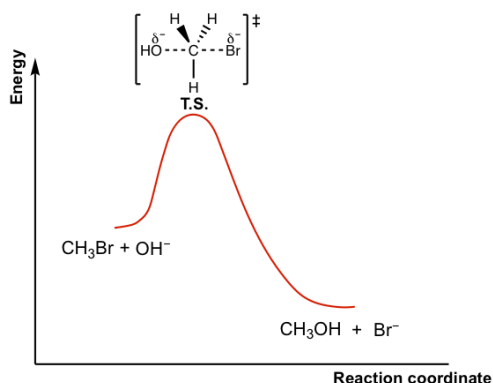


Fig. 7.1 Energy Diagram for S_N2 reaction between CH_3Br and OH^-

The top of the curve corresponds to the **transition state**, which is the highest-energy structure involved in the reaction. Transition state always involves partial bonds, partially formed bond and partially broken bond, and therefore is very unstable with no appreciable lifetime. The transition state therefore can **never** been isolated. The structure of the transition states is usually shown in a square bracket with a double-dagger superscript.

The Effect of Alkyl Halide Structure on S_N2 Reaction Rate

For the discussions on S_N2 mechanism so far, we focused on the reaction of methylbromide CH_3Br . Other alkyl halides could undergo S_N2 reactions as well. The studies on the reaction rate for S_N2 indicate that the structure category of electrophilic carbon in alkyl halide affects the reaction rate dramatically.

Type of Alkyl Halide	Alkyl Halide Structure
Relative Rate	
Methyl	CH_3X
30 Primary (1°) $\text{RCH}_2\text{-X}$ 1 Secondary (2°)	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{CH-X} \\ \diagup \\ \text{R}' \end{array}$
0.03 Tertiary (3°)	
(no S_N2 reaction)	$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{R}'' \end{array}$
negligible	

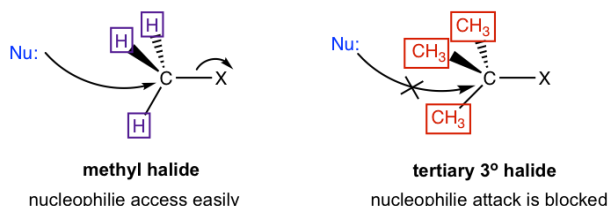
Table 7.1 Relative Reaction Rate of S_N2 for Different Type of Alkyl Halide

As shown in **Table 7.1**, methyl and primary halides are the substrates with the highest rate, the rate decreases a lot for secondary halides, and the tertiary halides do not undergo S_N2 reaction at all because the rate is too low to be practical.

The **relative reactivity of alkyl halides towards S_N2 reaction** can therefore be summarized as:

methyl > primary 1° > secondary 2° >> tertiary 3°
 too unreactive
 to undergo S_N2
 reaction

Why the trend is like this? This can be explained by the mechanism of S_N2 reaction. Actually this is one of the experiment evidences scientists based on for proposing the mechanism. A key feature in S_N2 mechanism is that the **nucleophile attacks from the back side**. When nucleophile approaching to the carbon, it is easiest to getting close to the methyl carbon because the hydrogen atoms connected on carbon are small in size. With the size of the groups connected on the carbon getting larger, it is becoming more difficult to access to the carbon, and such approaching is totally blocked for tertiary carbon with three bulky alkyl groups connected. Therefore, the reactivity difference is essentially caused by the **steric effect**. **Steric effect** is the effect that based on the steric size or volume of a group. Because of the steric hinderance of bulky groups on the electrophilic carbon, it is less accessible for nucleophile to do back-side attack, so the S_N2 reaction rate of secondary (2°) and tertiary (3°) substrates decreases dramatically. Actually the 3° substrates never go with S_N2 reaction mechanism because the reaction rate too slow.



The Stereochemistry of S_N2 Reaction

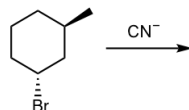
Another feature of S_N2 reaction mechanism is that the overall configuration of the carbon in the product get inverted comparing to that of the reactant, like an umbrella flipped inside out. Such inversion of configuration is called *Walden inversion*. let's see what is the stereochemistry consequence for such inversion.

Start with the (**R**)-2-bromobutane, the S_N2 reaction produces only one enantiomer of 2-butanol product, and it is predictable that the configuration of the product supposed to be **S** because of the configuration inversion.

Note: Inversion means the arrangement of the groups get inverted, not necessary means the absolute configuration, R/S, inverted. The product does get inverted R/S configuration comparing to the reactant for lot cases, but not guaranteed. The actual configuration of the product has to be determined accordingly.

Exercises 7.1

Show the product of the following S_N2 reaction (CN⁻ is the nucleophile):



Answers to Practice Questions Chapter 7

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