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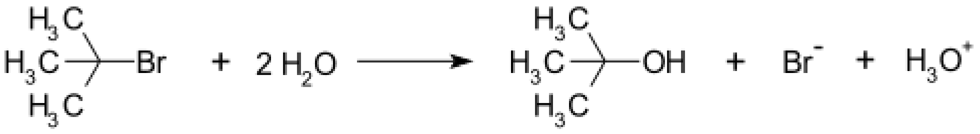
S_N1 reaction

The **S_N1 reaction** is a substitution reaction in organic chemistry, the name of which refers to the Hughes-Ingold symbol of the mechanism. "S_N" stands for "nucleophilic substitution", and the "1" says that the rate-determining step is unimolecular.[1][2] Thus, the rate equation is often shown as having first-order dependence on electrophile and zero-order dependence on nucleophile. This relationship holds for situations where the amount of nucleophile is much greater than that of the intermediate. Instead, the rate equation may be more accurately described using steady-state kinetics. The reaction involves a carbocation intermediate and is commonly seen in reactions of secondary or tertiary alkyl halides under strongly basic conditions or, under strongly acidic conditions, with secondary or tertiary alcohols. With primary and secondary alkyl halides, the alternative S_N2 reaction occurs. In inorganic chemistry, the S_N1 reaction is often known as the *dissociative mechanism*. This dissociation pathway is well-described by the cis effect. A reaction mechanism was first proposed by Christopher Ingold et al. in 1940.[3] This reaction does not depend much on the strength of the nucleophile unlike the S_N2 mechanism. This type of mechanism involves two steps. The first step is the reversible ionization of alkyl halide in the presence of aqueous acetone or ethyl alcohol. This step provides a carbocation as an intermediate.

Contents

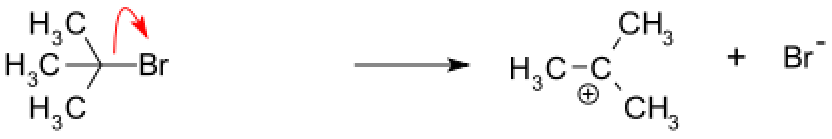
Mechanism

An example of a reaction taking place with an S_N1 reaction mechanism is the hydrolysis of tert-butyl bromide forming *tert*-butanol:

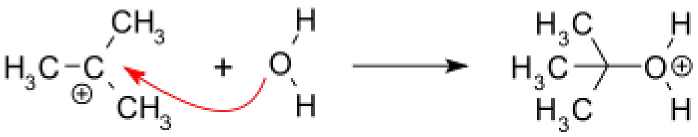


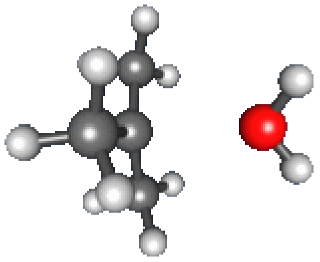
This S_N1 reaction takes place in three steps:

- Formation of a *tert*-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom: this step is slow and reversible.[4]



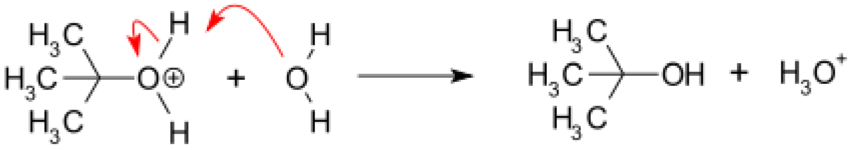
- Nucleophilic attack: the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i.e. a solvent) a third step is required to complete the reaction. When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.





Recombination of carbocation with nucleophile

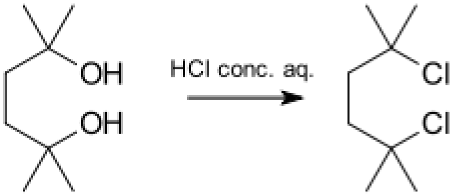
- Deprotonation: Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.



Scope

The S_N1 mechanism tends to dominate when the central carbon atom is surrounded by bulky groups because such groups sterically hinder the S_N2 reaction. Additionally, bulky substituents on the central carbon increase the rate of carbocation formation because of the relief of steric strain that occurs. The resultant carbocation is also stabilized by both inductive stabilization and hyperconjugation from attached alkyl groups. The Hammond–Leffler postulate suggests that this too will increase the rate of carbocation formation. The S_N1 mechanism therefore dominates in reactions at tertiary alkyl centers.

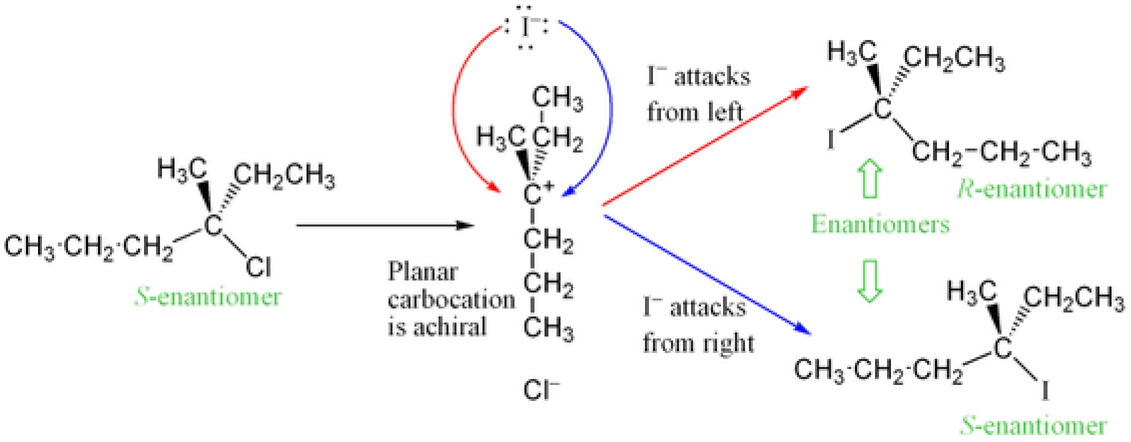
An example of a reaction proceeding in a S_N1 fashion is the synthesis of *2,5-dichloro-2,5-dimethylhexane* from the corresponding diol with concentrated hydrochloric acid:[5]



As the alpha and beta substitutions increase with respect to leaving groups the reaction is diverted from S_N2 to S_N1.

Stereochemistry

The carbocation intermediate is formed in the reaction's rate determining step is an *sp*^{2} hybridized carbon with trigonal planar molecular geometry. This allows two different ways for the nucleophilic attack, one on either side of the planar molecule. If neither way is preferentially favored, these two ways occur equally, yielding a racemic mixture of enantiomers if the reaction takes place at a stereocenter.[6] This is illustrated below in the S_N1 reaction of S-3-chloro-3-methylhexane with an iodide ion, which yields a racemic mixture of 3-iodo-3-methylhexane:



However, an excess of one stereoisomer can be observed, as the leaving group can remain in proximity to the carbocation intermediate for a short time and block nucleophilic attack. This stands in contrast to the S_N2 mechanism, which is a stereospecific mechanism where stereochemistry is always inverted as the nucleophile comes in from the rear side of the leaving group.

Side reactions

Two common side reactions are elimination reactions and carbocation rearrangement. If the reaction is performed under warm or hot conditions (which favor an increase in entropy), E1 elimination is likely to predominate, leading to formation of an alkene. At lower temperatures, S_N1 and E1 reactions are competitive reactions and it becomes difficult to favor one over the other. Even if the reaction is performed cold, some alkene may be formed. If an attempt is made to perform an S_N1 reaction using a strongly basic nucleophile such as hydroxide or methoxide ion, the alkene will again be formed, this time via an E2 elimination. This will be especially true if the reaction is heated. Finally, if the carbocation intermediate can rearrange to a more stable carbocation, it will give a product derived from the more stable carbocation rather than the simple substitution product.

Solvent effects

Since the S_N1 reaction involves formation of an unstable carbocation intermediate in the rate-determining step, anything that can facilitate this will speed up the reaction. The normal solvents of choice are both *polar* (to stabilize ionic intermediates in general) and *protic solvents* (to solvate the leaving group in particular). Typical polar protic solvents include water and alcohols, which will also act as nucleophiles and the process is known as solvolysis.

The **Y scale** correlates solvolysis reaction rates of any solvent (**k**) with that of a standard solvent (80% v/v ethanol/water) ($\mathbf{k_0}$) through

$$\log\left(\frac{k}{k_0}\right) = mY$$

with **m** a reactant constant (m = 1 for *tert*-butyl chloride) and **Y** a solvent parameter.[7] For example, 100% ethanol gives Y = −2.3, 50% ethanol in water Y = +1.65 and 15% concentration Y = +3.2.[8]

See also

- Arrow pushing
- Nucleophilic acyl substitution
- Neighbouring group participation
- S_N2 reaction

References

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External links

- Diagrams (http://www.chemhelper.com/sn1.html): Frostburg State University
- Exercise (https://web.archive.org/web/20030708024541/http://www.usm.maine.edu/~newton/Chy251_253/Lectures/Sn1/Sn1FS.html): the University of Maine

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