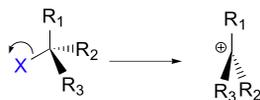
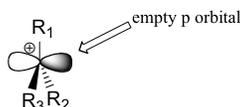


## 6.15: Energy Diagram for a Two-Step Reaction Mechanism

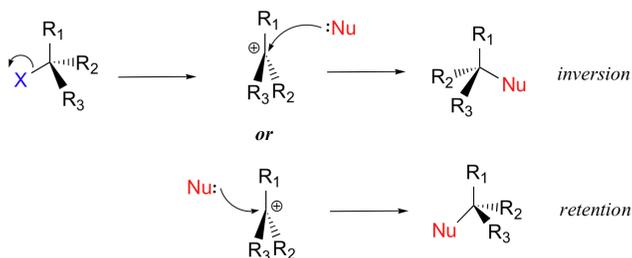
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S<sub>N</sub>1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as  $sp^2$  hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three  $sp^2$  hybrid orbitals is an empty, unhybridized  $p$  orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry'  $p$  orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.



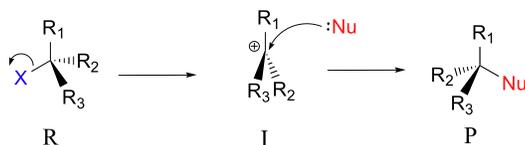
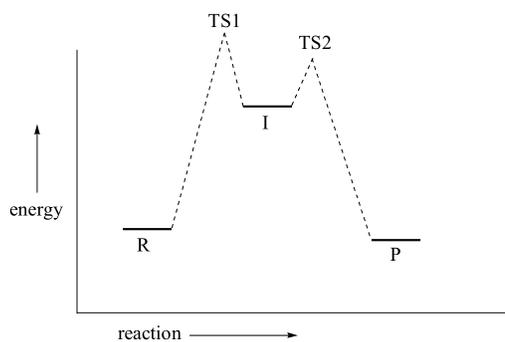
We saw that  $S_N2$  reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of  $S_N1$  reactions? In the model  $S_N1$  reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar,  $sp^2$ -hybridized carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an  $S_N1$  reaction with water as the incoming nucleophile.



### Exercise

Draw the structure of the intermediate in the two-step nucleophilic substitution reaction above.

The  $S_N1$  reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity. Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discrete bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the  $S_N1$  reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an  $S_N1$  reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



### Exercise

Draw structures representing TS1 and TS2 in the reaction above. Use the solid/dash wedge convention to show three dimensions.

Recall that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for the first step is higher than that for the second step. Also recall that an  $S_N1$  reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding

[Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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