

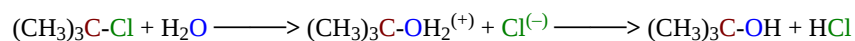
7.10: Two Mechanisms for Nucleophilic Substitution

The S_N2 Mechanism

As described in the previous section, a majority of the reactions thus far described appear to proceed by a common single-step mechanism. This mechanism is referred to as the S_N2 mechanism, where **S** stands for **S**ubstitution, **N** stands for **N**ucleophilic and **2** stands for **b**imolecular. Other features of the S_N2 mechanism are inversion at the alpha-carbon, increased reactivity with increasing nucleophilicity of the nucleophilic reagent and steric hindrance to rear-side bonding, especially in tertiary and neopentyl halides. Although reaction 3 exhibits second order kinetics, it is an elimination reaction and must therefore proceed by a very different mechanism, which will be described later.

The S_N1 Mechanism

Reaction 7, shown at the end of the previous section, is clearly different from the other cases we have examined. It not only shows first order kinetics, but the chiral 3°-alkyl bromide reactant undergoes substitution by the modest nucleophile water with extensive racemization. In all of these features this reaction fails to meet the characteristics of the S_N2 mechanism. A similar example is found in the hydrolysis of tert-butyl chloride, shown below. Note that the initial substitution product in this reaction is actually a hydronium ion, which rapidly transfers a proton to the chloride anion. This second acid-base proton transfer is often omitted in writing the overall equation, as in the case of reaction 7 above.



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