

Comparison of the Mechanisms of Substitution Reactions (S_N1 and S_N2) in Alkyl Halides

	S_N1	S_N2
Kinetics and Rate Law	First Order: Rate = $\kappa[R-X]^1$	Second Order: Rate = $\kappa[R-X]^1[Nu:]^1$
Rate determining Step	Formation of carbocation	Penta-coordinated carbon transition state
Characteristics of Mechanism	<p>Two steps:</p> <p>Step 1: $R-X \xrightarrow{\text{RDS}} R^+ + X^-$</p> <p>Step 2: $Nu:^\ominus + R^+ \longrightarrow R-Nu$</p> <p>1st step is the slow step. (Bond breakage)</p>	<p>One step:</p> <p>$Nu:^\ominus + R-X \longrightarrow R-Nu + X^-$</p> <p>Back attack. Simultaneous bond breaking and bond forming.</p>
Effect of alkyl structure on rate	<p>Stability of carbocation:</p> $R_3C^+ > R_2HC^+ > RH_2C^+ \gg H_3C^+$ <p>Alcohols are good substrates for S_N1 reactions when treated with HX. Water is a good leaving group.</p>	<p>Steric hindrance plays an important role in the reaction rate.</p> $CH_3X > RCH_2X > R_2CHX \gg R_3CX$
Effect of nucleophile on rate	<p>The rate of the reaction is independent on nucleophile concentration.</p> <p><i>Solvolysis is the typical S_N1 reaction, that is, the solvent -usually protic - serves as the nucleophile.</i></p>	<p>The rate of the reaction is dependent on the nature and concentration of the nucleophile.</p> <p><i>Strong nucleophiles/weak bases are preferred.</i></p>
Effect of solvent on rate	<p>The rate of the reaction increases with solvent polarity.</p> $H_2O > HCOOH > CH_3OH > CH_3COOH$ <p>Solvent reduces electrostatic interaction in the transition state.</p>	<p>Polar aprotic solvents provide a faster rate. The nucleophile is not solvated in polar aprotic solvents, which make them better nucleophiles.</p>
Possible rearrangements	Intermediate carbocations can rearrange, especially 2° to 3°.	There are no rearrangements