

Second order kinetics

A second order reaction in component A has a time-dependence given by

$$d[A]/dt = -k[A]^2$$

The integrated rate law is given by

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t k dt \text{ or } \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

This can be expressed as $[A] = [A]_0/(1 + [A]_0kt)$

Second order kinetics: the half life

The half life, $\tau_{1/2}$ occurs when $[A] = [A]_0/2$

$$\frac{1}{[A]_0/2} - \frac{1}{[A]_0} = k\tau_{1/2}$$

$$\tau_{1/2} = \frac{1}{k[A]_0}$$

For a second order process, the half life depends on the initial concentration $[A]_0$.

An important example of second order kinetics

A reaction that occurs in solution that is first order in two reactants is second order overall.

$$d[A]/dt = -k[A][B] , d[B]/dt = -k[A][B]$$

If the reaction has the stoichiometry $A + B \rightarrow P$ the concentrations follow

$$kt = \frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]/[B]_0}{[A]/[A]_0} \right)$$

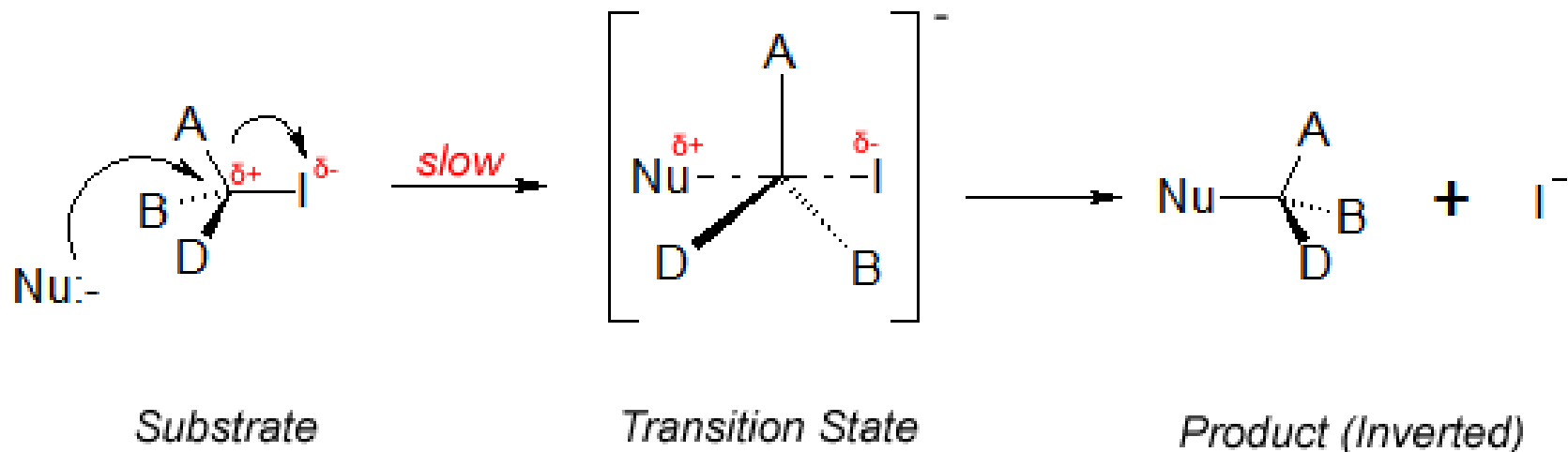
Integrated rate law for second order reaction $A + B \rightarrow P$

The time course for the appearance of product is given the integrated rate law:

$$[P] = \frac{[A]_0[B]_0 \left(1 - \exp\{([B]_0 - [A]_0)kt\} \right)}{[A]_0 - [B]_0 \exp\{([B]_0 - [A]_0)kt\}}$$

Note that the half-life for a second order process depends on the initial concentration of A and B.

S_N2 reactions



The net effect of a S_N2 reaction is that a leaving group is displaced by an attacking group (nucleophile). The process is inherently second order since the nucleophile must collide with the substrate in the rate-limiting step (labeled as slow above).

S_N2 reactions

The rate law of a S_N2 reaction can be written as:

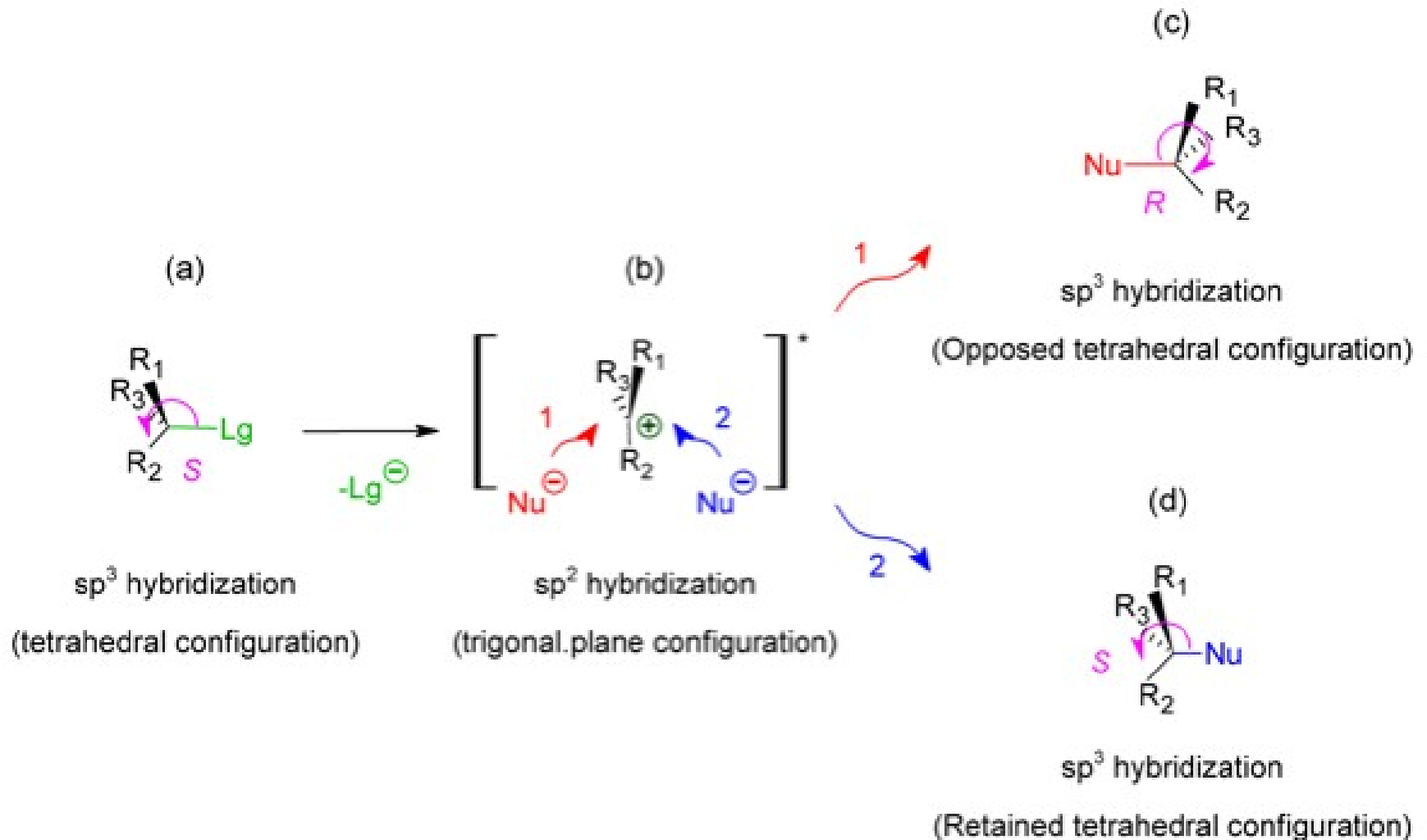
$$\text{rate} = k[\text{substrate}][\text{nucleophile}]$$

Reaction is favored in polar aprotic solvents. The reason for this is that the transition state is polar. It inherently involves a five coordinate intermediate with different polarity of attacking and leaving groups.

This rate law can be contrasted with that of the S_N1 reaction. In the S_N1 case the rate limiting step is the dissociation of the Tetrahedral carbon center to yield a three-coordinate carbocation. The attack by the nucleophile is rapid, so that the rate law is:

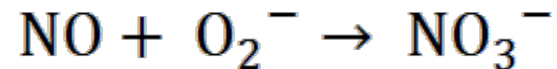
$$\text{rate} = k[\text{substrate}]$$

S_N1 reactions



Bimolecular reaction example

The reaction of NO with O_2^- (superoxide anion) is an example of a second order reaction with a great biological significance. The reaction is:



The bimolecular rate constant has been determined to be $k = 6.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. The reaction is important since the ratio of

$$\frac{[NO]}{[NO_3^-]}$$

is a crucial indicator of health. If this ratio is > 4 an individual is healthy. As this ratio falls to < 1 it indicates poor health.