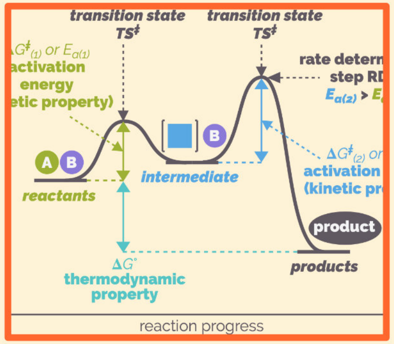
HIGHLIGHTS

- Reaction mechanisms & elementary steps
- Reaction profiles
- Reactants, transition states, intermediates & products
- Activation energy & the rate determining step
- Hammond postulate
- Rate expressions (or laws) & the number of molecules in a rate determining step



There are lots of reasons the rates of reactions and kinetics is important. How long pharmaceuticals stay in the body before being either broken down or excreted is an obvious example. Similarly, the lifetime of herbicides and pesticides in the environment is of vital importance. The rate these are broken down can have devastating consequences. Many of the reactions that we require to keep our bodies functioning are too slow to be of use without enzymes accelerating them. To truly appreciate synthesis you need to understand the mechanism and this can only be determined through kinetics. The list of why we should have a vague appreciation of kinetics is huge. Hopefully, I will not make too many mistakes and so this will be a useful introduction. Actually, I hope someone else has taught you properly and this is just a reminder ...

CHEMISTRY CLASSICS

RATES OF REACTION 2

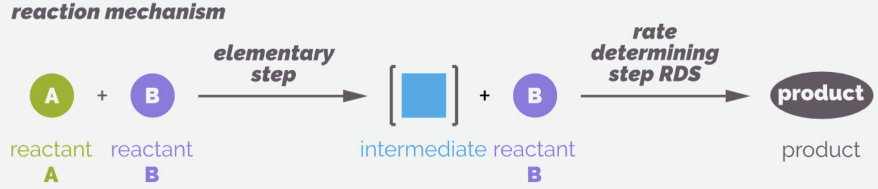
AN ORGANIC CHEMIST'S LOOK AT RATE EQUATIONS

Rates of reaction (simplified by an organic chemist)

Making Molecules www.makingmolecules.com

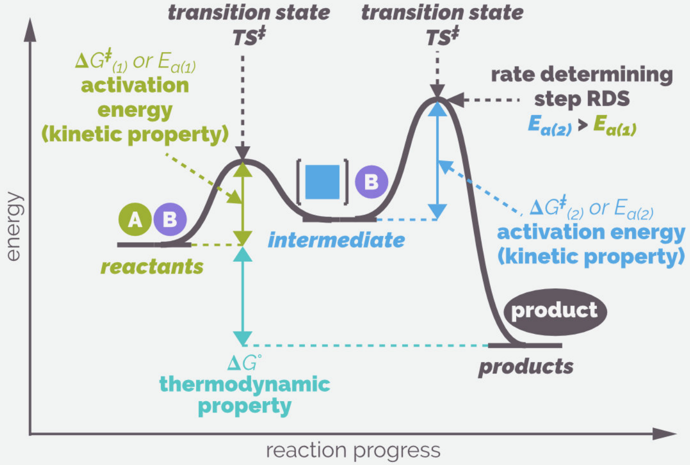
1. Reaction profile & reaction mechanisms

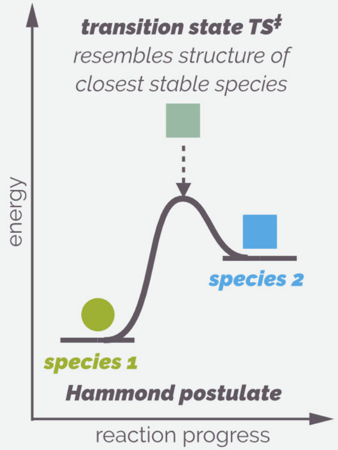
reaction mechanism



Reactant - starting materials or reagents
Intermediate - chemical species formed in one elementary step & consumed in the next
Product - final chemical species in sequence
Reaction mechanism - sequence of elementary steps that leads from reactants to products
Elementary step (reaction) - a reaction where reactants are directly converted to products with no intermediates (has a single transition state)
Rate determining step (RDS) - slowest elementary step in a reaction mechanism. It controls the rate

reaction profile





Reaction profile - visualization of the energy changes during a chemical reaction
Gibbs free energy ΔG° - thermodynamic property, negative value means reaction spontaneous
Transition state - saddle point on reaction profile. Each elementary step has a single transition state. It has no lifespan & reaction only passes through. Perfect alignment of atoms & partial bonds.
Activation energy $\Delta G^\ddagger$ - Minimum energy for reaction to occur. Saddle point on reaction profile (difference in energy between reactants & transition state or activated complex)
Intermediate - local energy minimum. Fleetingly stable species, it is highly reactive. It has a lifespan and will have a transition state on either side.
Rate determining step (RDS) - corresponds to elementary step with highest activation energy. Controls rate of reaction as this is minimum energy molecules must have.
Hammond postulate - as transition states cannot be isolated, the structure must be estimated. Hammond postulate states that two consecutive species in a reaction profile resemble each other if they have similar energy (there is little reorganization of the molecular structure)

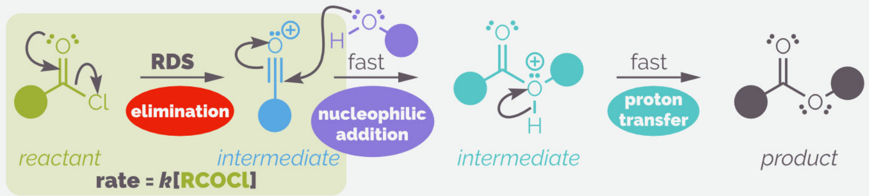
2. Rate equations

general rate equation (empirical expression)

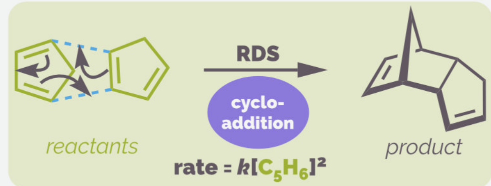
rate = $k[A]^a[B]^b$

rate of reaction = change in conc. per unit time
k = the rate constant (correction factor)
[A] = concentration of reactant A
a = order of reaction with respect to reactant A
(a+b) = overall order of reaction

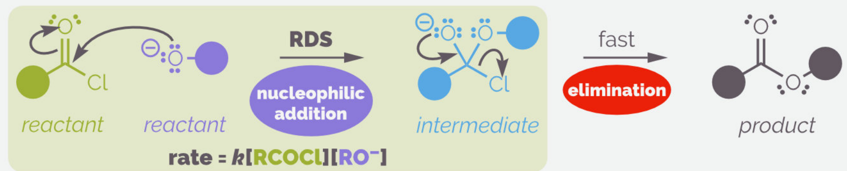
first order reaction: rate = k[RCOCl] - one molecule in RDS



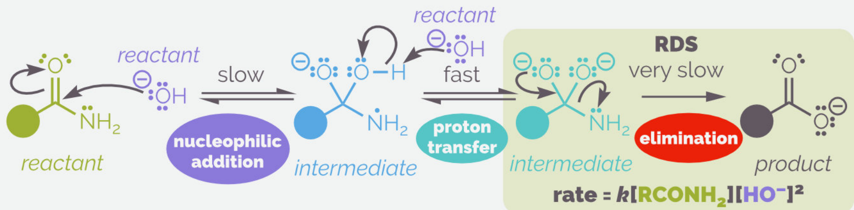
second order reaction: rate = k[C_5H_6 ***]²*** - two molecules in RDS



second order reaction: rate = k[RCOCl][RO–] - two molecules in RDS



third order reaction: rate = k[$RCONH_2$ ***][HO–]²*** - one molecule in RDS



Rate of reaction determined by the collapse of the tetrahedral intermediate. You do not know the concentration of this species so the rate equation must be given in terms of the reactants. This can be determined by assuming initial steps are equilibria & using equilibrium expressions. Here the rate constant k can be thought to contain two equilibrium constants as well. The full working will be on the MakingMolecules website.