Chem 116 Lecture 14 Notes
10/21/08 (LL)

iClicker Question

Answer C
Rate = $k[CO_2]^2 [O_2]$

Key points about kinetics so far

Collision Theory= For chemicals to react they must collide. The collisions also have to occur at correct orientation

Depends on: Temperature, activation energy, and fraction of collisions that occur at the right orientations of the molecules

Reaction Pathway
Transition state (Activated complex)- Intermediate state between reactants and products where the energy is the highest

Relating energy profiles, activation energies, and speeds of reactions
Activation energy determines the speed of reactions - if the activation energy is higher, the speed is slower

Fastest reaction- Lowest E_a
Slowest reaction- Highest E_a

Ranking the reactions in order from fastest to slowest, if the reactions occur at the same temperature and have the same value for A (related to the fraction of collisions at the right orientation)
1, E_a = 15 kJ/mol (fastest)
3, E_a = 20 kJ/mol
2 E_a = 24 kJ/mol (slowest)

Reversing Energy Profile
Rxn 3 is the fastest because it has the lowest E_a

Elementary Reactions
Molecularity- How many particles are involved in the elementary step occurring
How many particles involved in elementary step

A→B rate = k [A] – Unimolecular
2A → C = rate $[A]_2$ - Bimolecular 2 A colliding
A = B → D = rate [A] [B] – Bimolecular A+ B Colliding

Rate Determining Step – Determines how fast reaction goes, reaction only goes as fast as the slowest step

Slow step – Rate determining step

Intermediates – Chemicals that show up on reactant and product side - they get created in one step of the mechanism and then used up again in another step

Fast Equilibrium – Forward and reverse reaction happen at the same rate, and equilibrium gets established faster then the rate determining step

Sample Exercise 14.15 p 606

Step 1:
$2NO_2Cl + Cl \rightarrow 2NO_2 + Cl + Cl_2$
Intermediates – Cl
$2NO_2Cl \rightarrow 2NO_2 + Cl_2$
Condition 1 adds up to overall reaction

Condition 2- Doesn't add up
Rate = K_2 $[No_2 Cl]$ $[Cl]$

Fast reversible has forward rate = reverse rate of that step
Step 2
$NO_2Cl \leftrightarrows NO_2 + Cl$

Forward rate = Reverse rate

$k_f [NO_2Cl] = k_r [NO_{2]} [Cl]$

- Want to solve for Cl, substitute into overall reaction rate & see if it makes overall reaction rate the same as the experimentally observed rate law

$[Cl] = k_f [NO_2Cl] / k_r [NO_{2]}$

Rate = $k_2 [NO_2Cl] [Cl]$

$k_2 [NO_2Cl] (k_f [NO_2Cl] / k_r [NO_{2]})$

Combined (k_2 k_f / k_r) :

$[NO_2Cl]_2 / [NO_2]$

-Now it is the same as the experimentally determined rate law