Q6 → recheck
[high energy cost to keep
≡ weak binding]

NAME: ___Sukant Koal___   ENTRY #: _2015CHI0190_

1.5

1) "The rate of a chemical reaction is determined by the number of molecular collisions with sufficient energy *and* with the proper orientation in a given period of time", as summarised below:

Rate of reaction = $\dfrac{\text{Number of collisions}}{\text{Unit of time}}$ × Fraction with sufficient energy × Fraction with proper orientation
[A]   [B]   [C]

Of the three factors [A], [B] and [C], which factor(s) do catalysts influence when they accelerate reaction rates? Explain your answer.

[B] :

ΔG

uncatalysed
Ea uncat
Ea catalysed
R
P
rxn coord

proper orientation

Catalysts stabilise the TS‡ and decrease the [B] activation energy necessary.

They do not increase energy of the molecules, they make it possible for molecules w/ lower energies to react ⇒ fraction of molecules increase

[A]: Because the catalyst binds to the ground state, it decreases the number of collisions / unit time that take place, but the increase in [B] more than compensates for decrease in [A]   [2]

2) "**Effective molarity** is the concentration of the reactant that would be required in an *intermolecular* reaction for it to have the same rate as the *intramolecular* reaction". Is this statement true or false? Justify your answer.

True ✓ Effective molarity tells the concentration that of reactant would be needed for the pseudo first order / intermolecular (second order) reaction to achieve the same rate as the first order intramolecular reaction. ✓ given that the same bond making / bond breaking events take place. As EM is the ratio of rate constants and rate constant directly depend on reactant concentration   [2]

1st order / 2nd order

3) Arrange compounds I, II and III in order of increasing Effective Molarity (EM) to be expected for the intramolecular cyclisation shown below. Explain your answer.

Scheme:

Intra-molecular cyclisation

Molecule #	Structure
I	X = Y = Z = H
II	X = Y = CH$_3$; Z = H
III	X = Y = Z = CH$_3$

Order of EM:

Effective Molarity	Lowest	Intermediate	Highest
Molecule Number	1	3	2

I   II   III

3) Explanation:

Em for 2 & 3 will be higher than 1 because the presence of the two Me groups on N ~~will~~ create a steric compression that push the molecule closer to the transition state and hence facilitate a faster reaction.

Em for 3 will be higher than 2 because the Me group on the C adjacent to N will lead to steric hindrance and slow down the reaction, while 2 has a H in that position ⇒ no steric hindrance

[1, 2]

4) The graph below shows the <u>experimentally determined</u> dependence of effective molarity (M$_{eff}$; y axis) on 'linker length' 'n' (x axis) for the binding of a small molecule by a large molecule as depicted in the schematic diagram shown below.


constant, only the PROXIMITY varies

K_d^{intra}

K_d^{inter}

$M_{eff} = K_d^{inter} / K_d^{intra}$
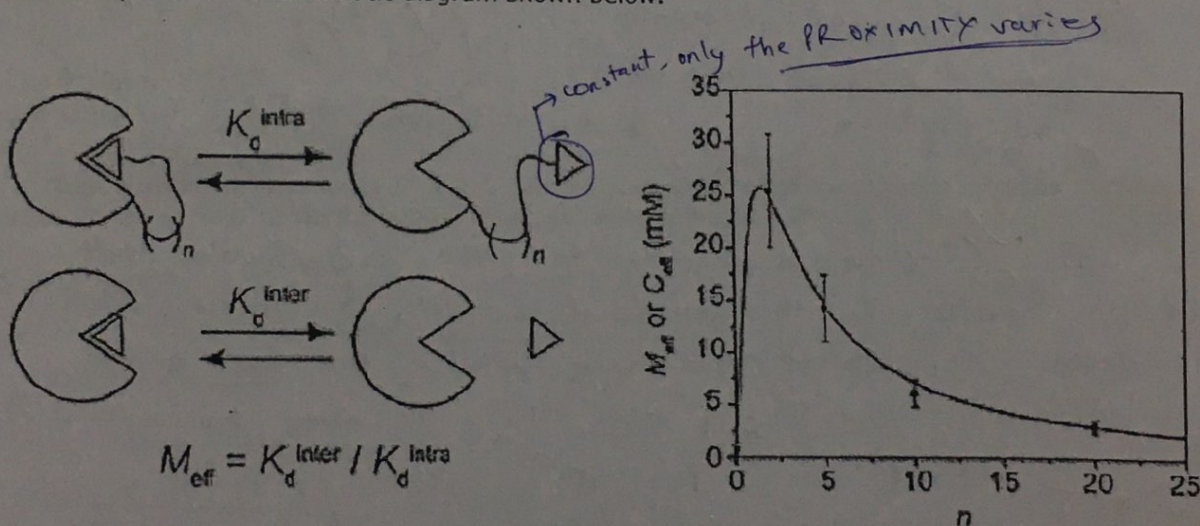
Does the graph have the 'expected' shape? Explain your answer.

~~No.~~ ~~with the linker length~~ ~~The graph should be closer to~~

n>0; Em should not increase with $^{Mem \; constant}$ linker length in the beginning as then the molecules are in closest proximity. Steric hindrance does not come into the picture as n is not the length of the entire chain

Explain the shape of the graph (i.e. explain why EM decreases as linker length increases).

As linker length increases, the stability of the $^{cyclic \; compd}$ ~~ring~~ that will formed decreases. ⇒ Em decreases ^{conformations}
$^{Proper \; orientation}$

Also, with increasing linker length, the intra ~~and~~ ~~the inter~~ reactions ~~to~~ gets closer to the inter reaction (electronic ~~effects~~ ↓) ⇒ Em decreases (ratio) [0.5, 1, 3] the rate

Intra reactions are faster partly because of PROXIMITY ~~Faster~~ Reactions rates vary with the time molecules spend within a critical distance proximity ↑ ⇒ EM ↓ [Reactant = const, only proximity varies]

5) Heterolysis of molecule X-Y in the absence of H_2O [Reaction I] as well as in the presence of H_2O [Reaction II] and [Reaction III] (where H_2O catalyses the heterolysis by stabilising incipient charge), is shown schematically below.

[Reaction I]
Heterolysis
(unsymmetrical bond breaking)

[Reaction II]
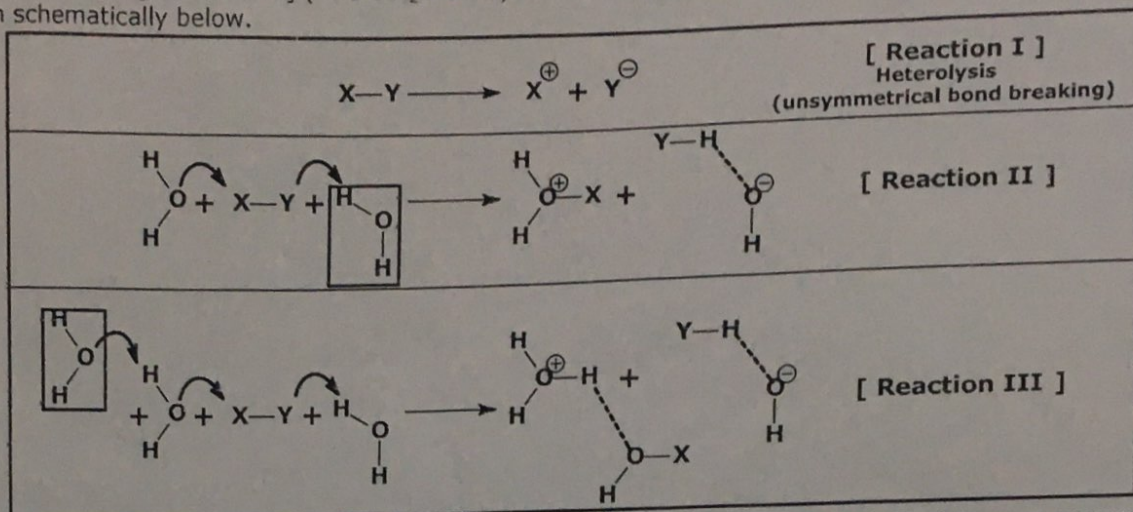
[Reaction III]

What type of catalysis does the boxed H_2O molecule carry out in each case? Explain your answer.

In Reaction II: _General acid catalysis_   **In Reaction III:** _Specific Base Catalysis_

Explanation: The water molecule protonates the substrate in the slow step.

Concn of this H_2O will appear in the rate law expression

The water molecule deprotonates the other water molecule, BUT THIS IS NOT THE SLOW STEP. This deprotonation occurs before rds, so this water molecule does not appear in the rate law expression

[2, 2]

6) *Three basic effects* determine the products formed in shape selective catalysis by zeolites.

For example:
Of all possible products, the molecule(s) with the **lowest free energy of formation** in the *adsorbed* phase will be preferentially formed.

This is an example of: ~~reaction shape selectivity~~ transition state shape selectivity

Explanation: lowest energy of formation ⟹ whatever transition state is leading to a product that ~~is~~ costs less energy to form is allowed to proceed.

Of all possible products, the molecule(s) with the **highest free energy of adsorption** will preferentially *desorb* and accumulate in the product state.

This is an example of: _product shape selectivity_

Explanation: Highest free energy of adsorption ⟹ more energy needed to keep it adsorbed in the zeolite pores as it is in the correct shape/orientation to leave ⟹ gets desorbed

Of all possible of reactants, those **that can fit inside a zeolite catalyst**, those with the lowest free energy of *adsorption* will be preferentially adsorbed and can then undergo reaction.

This is an example of: ~~transition state selectivity~~ reactant shape selectivity

Explanation: lowest free energy of adsorption ⟹ least energy cost to adsorb it into the zeolite pores and begin the reaction

+½

[1.5 x 3 = 4.5]