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22573

Model Answer Key for Physical Organic Chemistry

Q1. A. Explain the following terms (any five one mark to each right answer)

1. Polar covalent bond

A covalent bond that has an unequal sharing of the bonding pair of electrons is called polar covalent.

2. Heterogeneous catalyst

A heterogeneous catalyst is one that does not dissolve in the solution, and hence the catalysis takes place in a phase separate from the solution (typically the surface of the catalyst). An example is the reduction of olefins with H_2 catalysed by Pd/C .

3. Inductive effect

The phenomenon of withdrawing electrons through sigma bonds to the more electronegative atom or group is called an inductive effect.

4. Charge transfer complex

The complexes formed between the donor and acceptor are referred to as charge-transfer complexes. A donor-acceptor interaction or Charge transfer occurs between any two molecules, or regions of a molecule, where one has a low energy empty orbital (acceptor) and the other a high energy filled orbital (donor).

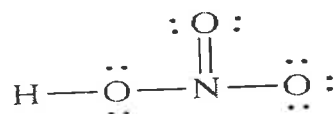
5. First order reaction

If the reaction rate has a linear dependence on a reactant's concentration, then we define the reaction as first order with respect to this reactant. For example, if the concentration of A is doubled and the rate doubles, then the reaction is first order with respect to A.

Q1. B. Fill in the blanks (any five one mark to each right answer)

1. Ground state electronic configuration for Magnesium is $1s^2 2s^2 2p^6 3s^2$.

2. Lewis structure for Nitric acid (HNO_3) is



3. ~~Formal charge on oxygen in hydroxide ion is -1~~ p-orbital

2

4. Tetracyanoethylene is an excellent acceptor, and it forms **charge-transfer complexes** with electron rich systems such as hexamethylbenzene.

5. The formula for calculation of half-life for first order reaction is

$$t_{1/2} = \frac{\ln(2)}{k}$$

$$t_{1/2} = 0.693/k$$

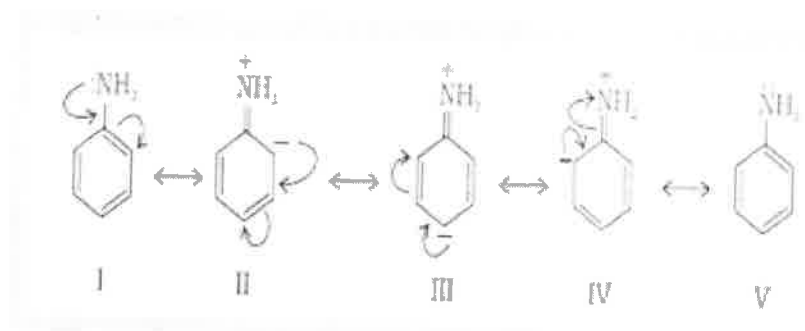
6. Crown ether is an example of **Phase transfer catalyst**.

Q1. B. Fill in the blanks (One mark each for correct pairing)

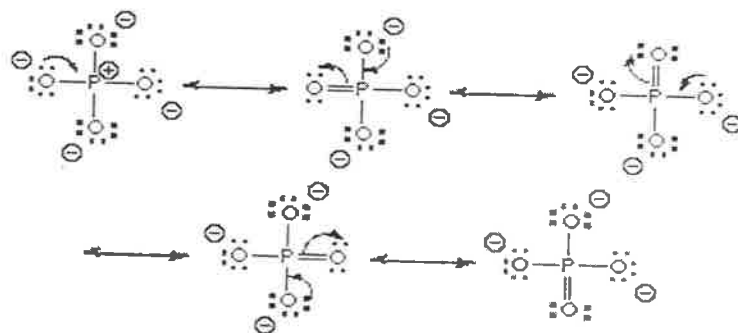
- | | |
|--------------------------------|--------------------------|
| 1. dx^2-y^2 | sigma symmetry |
| 2. Carbon in alkane | sp^3 hybridized |
| 3. Starch iodine complex | Charge transfer |
| 4. OH^- | example of specific base |
| 5. valence electron of Co (27) | $3d^7 4s^2$ |

Q2. A. Draw the resonating structures for (One mark each)

a.



b.



3

Q2. B. Draw Molecular orbital diagram for Ethane. Indicate HOMO and LUMO.

(3 Marks)

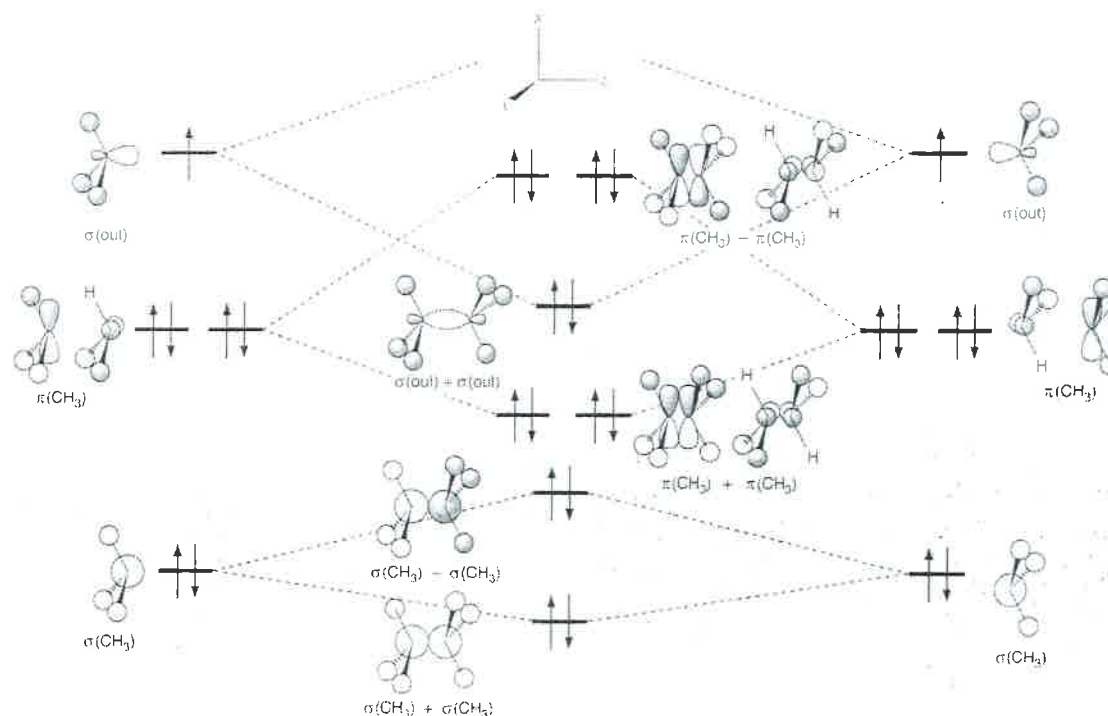


Figure 1.12

The orbital mixing diagram for the formation of ethane from two pyramidal CH_3 groups.

The computed MOs are shown in Figure 1.13.

HOMO $\rightarrow \pi\text{CH}_3 - \pi\text{CH}_3$ LUMO $\sigma\text{out CH}_3 - \sigma\text{out CH}_3$

Correct diagram carry 2 marks, 0.5 and 0.5 for HOMO and LUMO.

Q2. C. Fill in the blanks on the basis of Kinetic isotopic effect.

(3 Marks)

1. When k_H / k_D is greater than one, we call the isotope effect **normal**. When k_H / k_D is less than one, we call the isotope effect **inverse**. (0.5 and 0.5 Marks)

2. ~~The energy measured at the lowest point in the potential energy is referred to as the zero-point energy (ZPE).~~ (1 Mark) **Hydrogen**

3. ~~An alpha secondary isotopic effect occurs when the atom undergoing reaction has the associated isotope, whereas a beta secondary isotopic effect occurs when the neighbouring atom has the isotope.~~ (0.5 and 0.5 Marks)

Q2. D. Define turn over number. Explain metal ion catalysis with example. (3 Marks)

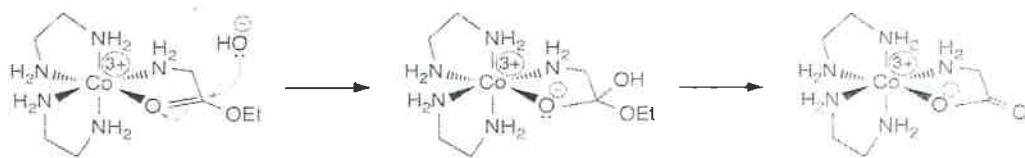
Definition 1 marks

The turnover number is average number of reactants that a catalyst acts upon before the catalyst loses its activity.

Relevant and systematic Explanation from content provided below give 2 Marks

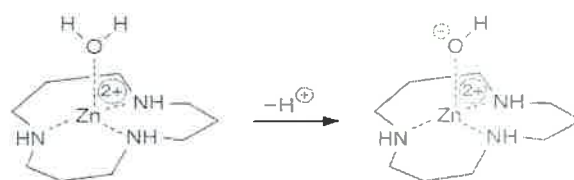
Metal Ion Catalysis

If formal charges and dipoles can stabilize charges on transition states, charges on metals can act similarly. Metal coordination can polarize bonds, thereby enhancing their inherent reactivity. Metals are common parts of enzymes, where coordination of a substrate to a metal leads to activation toward nucleophilic attack. As an example of metal ion catalysis, the hydrolysis of glycine ethyl ester by hydroxide is increased 2×10^6 -fold by coordination to (ethylenediamine) $_2\text{Co}^{3+}$ (Eq. 9.7). In the next chapter, we will also see that metals are essential parts of many common organic reagents. For example, lithium aluminum hydride requires the lithium to activate a carbonyl group toward nucleophilic attack by hydride (see Section 10.8.4).



(Eq. 9.7)

Another aspect of metal catalysis is the ability to create high concentrations of hydroxide at neutral pH. Water is a common ligand to a metal, and the binding between the water and metal typically withdraws electrons from the water, making it more acidic. For example, in the complex shown in Eq. 9.8, the pK_a of the metal-bound water is 7.2, over 10^8 more acidic than water itself. Deprotonation gives a metal-bound hydroxide that can act as a base or a nucleophile. An example of using the electrophilic nature of metals coupled with the presence of a hydroxide ligand is given in the Connections highlight on page 502.



(Eq. 9.8)

5

Q3. A. Give Eyring equation and Arrhenius rate law. State how they differ from each other. (3 marks)

Clearly name each term.

(1.5 marks for Eyring equation and Arrhenius rate law and 1.5 marks for difference)

Eyring equation is

1.5 mark for each term

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{(\Delta S^\ddagger / R)} e^{(-\Delta H^\ddagger / RT)}$$

$$= \kappa \left(\frac{k_B T}{h} \right) e^{(\Delta S^\ddagger / R)} e^{(-\Delta H^\ddagger / RT)}$$

Arrhenius rate law is

$$k = Ae^{(-E_a / RT)}$$

The Arrhenius equation arises from empirical observations of the **macroscopic rate constants** for a particular conversion, such as A going to B by various paths. It is **ignorant of any mechanistic considerations**, such as whether one or more reactive intermediates are involved in the overall conversion of A to B.

The Eyring equation analyzes a **microscopic rate constant for a single-step conversion** of a reactant to a product. In a **multistep process involving reactive intermediates**, there is an Eyring equation and thus a free energy G^\ddagger for each and every step. In contrast, **E_a describes the overall transformation.**

Q3. B. Calculate rate constant in hr⁻¹ for the reaction with halflife 360 min.

(2 marks)

Conversion (0.5 Mark)

1 hour is 60 min

So 360 min is 6 hours

Formula (0.5 Mark)

$$K = 0.693 / t_{1/2}$$

$$K = 0.693 / 6$$

$$= 0.115 \text{ hr}^{-1} \text{ (answer with unit 1 mark)}$$

6
Mention symmetry elements of MH_3

Q3. C. Define group orbital. Compare the energy of linear and bent form of MH_2 system using molecular orbital diagram. (3 Marks)

(Definition 1 mark and diagram 2 marks)

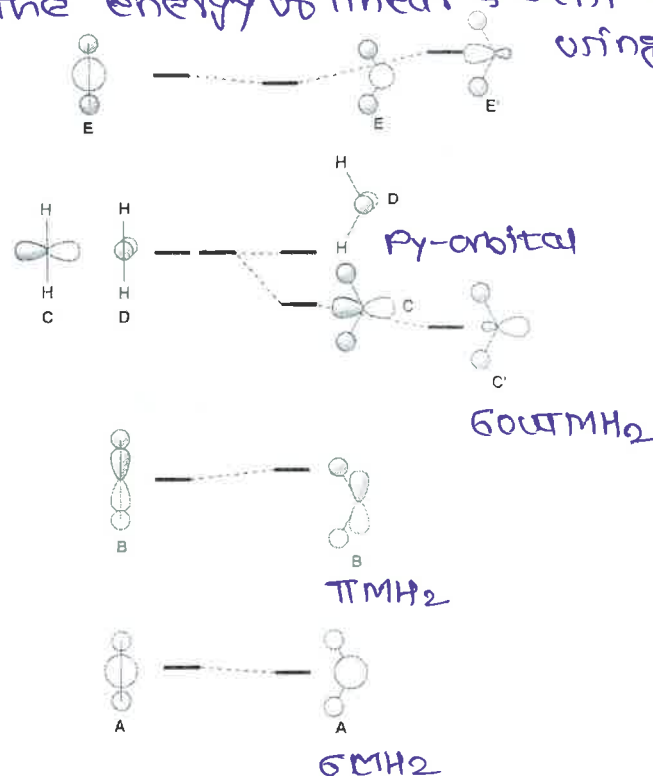
System. Enlist molecular orbital for ammonia

Group orbitals-orbitals that are delocalized only over a defined group of atoms. OR

A collection of partially delocalized orbitals that is consistently associated with a functional group

or similar collection of atoms in molecules.

Q3D → compare the energy of linear & bent form of MH_2 system using MO diagram.



Q3. D. Why Pyramidal form of MH_3 system is more stable than planar form? (3 marks)

Diagram is not expected, student should include following points in his answer.

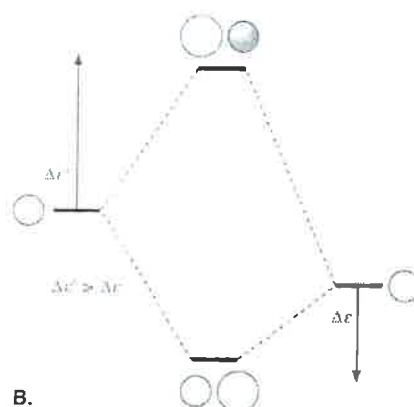
1. On pyramidalization, the energy of A will change very little. Perhaps a slight energy lowering will occur because the hydrogens are closer to each other and can interact favorably.
2. The B/C pair will rise in energy on pyramidalization significantly more than A is lowered because of the greater directionality of the bonding. In the planar form the p orbitals can point more directly at the hydrogens, maximizing overlap. This overlap diminishes as the system distorts, and this destabilizes the orbitals. Even with distortion, the B/C pair of orbitals remains degenerate.
3. The biggest effect by far of pyramidalization is on orbital D. A formerly nonbonding orbital becomes significantly bonding. The hydrogens have moved off the node of the p orbital, allowing favorable bonding interactions to develop. Thus, the energy of D is considerably lower in pyramidal vs. planar methane.

2

Q4. **What do you mean by second order mixing? State any four rules of QMOT. (3)**

The mixing of orbitals of different energy (nondegenerate) is called second order mixing.

(1 mark)



The Rules of QMOT*

1. Consider valence orbitals only.
2. Form completely delocalized MOs as linear combinations of s and p AOs.
3. MOs must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule.
4. Compose MOs for structures of high symmetry and then produce orbitals for related but less symmetric structures by systematic distortions of the orbitals for higher symmetry.
5. Molecules with similar molecular structures, such as CH_4 and NH_3 , have qualitatively similar MOs, the major difference being the number of valence electrons that occupy the common MO system.
6. The total energy is the sum of the molecular orbital energies of individual valence electrons.
7. If the two highest energy MOs of a given symmetry derive primarily from different kinds of AOs, then mix the two MOs to form hybrid orbitals.
8. When two orbitals interact, the lower energy orbital is stabilized and the higher energy orbital is destabilized. The out-of-phase or antibonding interaction between the two starting orbitals always raises the energy more than the corresponding in-phase or bonding interaction lowers the energy.
9. When two orbitals interact, the lower energy orbital mixes into itself the higher energy one in a bonding way, while the higher energy orbital mixes into itself the lower energy one in an antibonding way.
10. The smaller the initial energy gap between two interacting orbitals, the stronger the mixing interaction.
11. The larger the overlap between interacting orbitals, the larger the interaction.
12. The more electronegative elements have lower energy AOs.
13. A change in the geometry of a molecule will produce a large change in the energy of a particular MO if the geometry change results in changes in AO overlap that are large.
14. The AO coefficients are large in high energy MOs with many nodes or complicated nodal surfaces.
15. Energies of orbitals of the same symmetry classification cannot cross each other. Instead, such orbitals mix and diverge.

*Adapted, with modifications, from Cimare, B. M. (1979), *Molecular Structure and Bonding: The Qualitative Molecular Orbital Approach*, Academic Press, New York

(Any four rules -2 marks, 0.5 each)



Q4. ^C Define fast kinetics. Enlist the method to study fast kinetics. Explain any one (3)

If the half-life for a reaction is just a few seconds or less, the reaction is typically completed within the time required to introduce and mix the reactants within the reaction vessel. To measure the rate of such reactions is called fast kinetics.

Following methods are used

Flow Techniques

Flash Photolysis

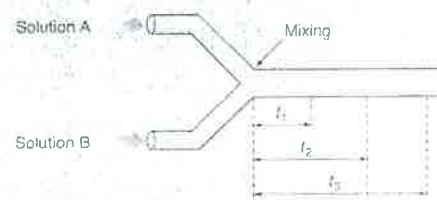
Pulse Radiolysis

Flow Techniques

When the rate of a reaction is faster than the time it takes us to introduce and mix reagents, we must turn to a method that achieves rapid mixing and has the ability to monitor the extent of reaction at various times. The most common methods involve flow tubes.

The reactants are mixed at the point where the two tubes intersect, and then the extent of reaction is followed by an analysis of the mixture at various points along the observation tube. The flow rate of the tube is known, so that the time from the point of mixing is known at each analysis point along the tube.

In the stopped-flow method, the flow is suddenly stopped at various times, and the analysis is performed at the same point in the observation tube at each different time. Several commercial versions of this apparatus are available for stopped-flow analyses, and it is a particularly common method for the analysis of enzyme-catalyzed reactions. With this technique reactions with half-lives as short as milli-seconds can be measured.



**Other methods can be refereed from Modern Physical Organic Chemistry Eric V. Anslyn
page no. 399-402**

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Q4. Q. What is phase transfer catalysis? Give examples (2)

Phase transfer catalysis involves enhancing the rates of reactions of ionic species such as nucleophiles and bases with organic molecules by the addition of a phase transfer agent.

The phase transfer agent is commonly a cationic surfactant or crown ether / cryptand. When using a surfactant, such as a tetraalkylammonium or tetraalkylphosphonium, the cationic group ion pairs with the reactive

anion and facilitates its transfer into the organic layer, where it is highly reactive. The use of crown ethers or cryptands leads to complexation of a Li^+ , Na^+ , or K^+ counterion of the anion, again facilitating its transfer into the organic layer.

Q3 C) Q4. D. Mention symmetry elements of MH_3 system. Enlist molecular orbitals for ammonia with number of electrons in each orbital. (3)

A trigonal planar structure with three equivalent ligands belongs to the point group called D_{3h} . The structure possesses a C_3 axis perpendicular to the plane of the molecule that passes through the central atom. It also possesses three C_2 axes perpendicular to the central C_3 axis, one along each M-H bond vector (only one is shown to the right). To possess a C_3 axis and a C_2 axis means that the molecule can be rotated along this axis by 120° and 180° , respectively, returning exactly the same structure with atoms returned to identical positions in space. A D_{3h} structure also possesses three internal mirror planes, called σ planes. They contain the C_3 axis and lie along each M-H bond (only one is shown), where reflection of the atoms through these mirror planes likewise gives back the same structure.

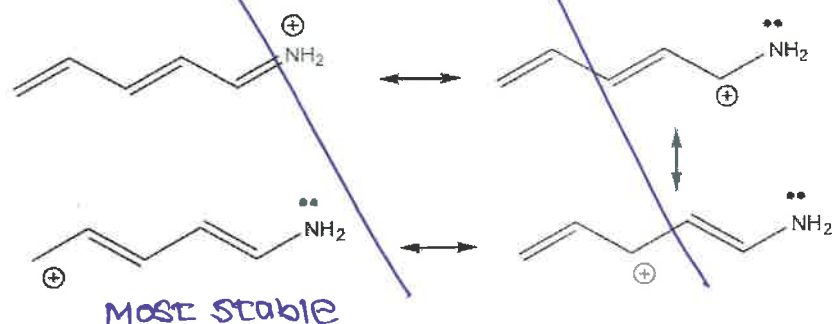
Molecular orbitals for ammonia with number of electrons in each orbital are

one Sigma (NH_3) 2 electrons

two Pi (NH_3) 4 electrons

one Sigma out (NH_3) 2 electrons

Q5. A. Draw resonating forms for following structure and Indicate most stable structure. (3)



Q5. B. Define reaction intermediate. Give example. Explain formation of any one. (3)

A reactive intermediate in organic chemistry is typically some form of carbon that either does not have the requisite four bonds, or has less than an octet of electrons, or is highly strained.

1. Carbocations Carbenium ions Carbonium ions
2. Carbanions
3. Radicals

1½ marks

Formation should be explained on the basis of MH3 system with number of electrons in each orbital. (1½ marks)

Q5. C. A first order reaction was found to have energy of activation of 2.15×10^4 J/mol. Calculate the temperature at which reaction will have a rate constant of 0.030 sec^{-1} . Frequency factor $A = 5 \times 10^{13} \text{ sec}^{-1}$ and $R = 8.314 \text{ J/kmol}$ (2)

Q5A → a)
b)
c)

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Formula

$$k = Ae^{-E_a/RT}$$

$$\log k = \log A - \frac{E_a}{RT \times 2.303}$$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$T = \frac{-E_a}{2.303 RT} \times \frac{1}{\log k} + \log A$$

$$= \frac{-2.15 \times 10^4}{2.303 \times 8.314 \times \log(5 \times 10^{-5})} + \log(5 \times 10^{-5})$$

$$= \frac{-2.15 \times 10^4}{2.303 \times 8.314 \times (-1.523)} + 13.70$$

$$= \frac{-2.15 \times 10^4}{29.16} + 13.70$$

$$= 737.51 + 13.70$$

$$T = 751.01 \text{ K}$$

Q5. D. Write a short note on Charge transfer complexes. (3)

Marks should be given on the basis of following content in answer and other relevant points

The complexes formed between the donor and acceptor are referred to as charge-transfer complexes. A large extent of charge transfer leads to colors. For example, tetracyanoethylene and hexamethylbenzene form a complex that is deep purple. No new bonds are formed, however, as each partner can be re-isolated intact. Further, tetracyanoethylene and tetrathiafulvalene crystallize as an almost black solid.

(2)

The color arises from an absorbance of light that promotes an electron from the donor to the acceptor the full charge transfer occurs in the excited state, while only "orbital mixing" occurs in the ground state.

A donor-acceptor interaction occurs between any two molecules, or regions of a molecule, where one has a low energy empty orbital (acceptor) and the other a high energy filled orbital (donor). When these two orbitals are aligned properly, some extent of charge transfer can occur from the donor to the acceptor. This is a stabilizing interaction.

A donor-acceptor interaction in that context was defined as a lone pair that could donate toward a low-lying empty orbital, possibly an antibonding orbital. A donor-acceptor binding interaction is another weak force that can be used to impart structure and hold compounds together.

Q6. A. Complete the following table on the basis of hybridization.

(3)

Molecule	Hybridized state of underlined atom	Bond angle
<u>S</u> F ₆	sp ³ d ² (0.5)	90° (0.5)
<u>C</u> H ₂ =CH ₂	sp ² (0.5)	120° (0.5)
<u>Be</u> Cl ₂	sp (0.5)	180° (0.5)

(0.5 For each correct answer)

Q6. B. Write a short note on general acid catalysis. (4)

Refer following page nos 507-510 from Modern Physical Organic chemistry Eric Anslyn

9.3.1 Specific Catalysis

The specific acid is defined as the protonated form of the solvent in which the reaction is being performed. For example, in water the specific acid is hydronium. In acetonitrile, the specific acid is CH₃CNH⁺, and in DMSO the specific acid is CH₃SO(H⁺)CH₃. The specific base is defined as the conjugate base of the solvent. As examples, in water, acetonitrile, and DMSO, the specific bases would be hydroxide, ⁻CH₂CN, and CH₃SOCH₂⁻, respectively. These definitions lead to strict definitions for specific catalysis. Specific-acid catalysis refers to a process in which the reaction rate depends upon the specific acid, *not* upon other acids in the solution. Specific-base catalysis refers to a process in which the reaction rate depends upon the specific base, *not* upon other bases in the solution. To understand the kinds of reaction mechanisms that would depend only upon the specific acid or base, we need to examine some possible mechanisms and the associated kinetic analyses.

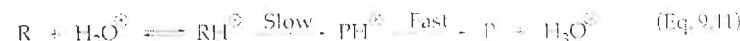
The Mathematics of Specific Catalysis

Let's start with an obvious example of specific-acid catalysis. We use water for demonstration purposes, but the kinetic development would be the same for other solvents. Eq. 9.11 shows a schematic mechanism in which hydronium protonates a reactant or substrate (R) prior to a reaction that is rate-determining. The slow step could be first order as shown in Eq. 9.11, or it commonly involves addition of a nucleophile that would then become part of the kinetic expression. Water is a common nucleophile. We keep the scenario simple here, because having additional reactants involved in the rate-determining step does not affect the conclusion we are leading to regarding the kinetic behavior found for the acid catalyst. After the reaction has proceeded, the proton is lost back to the solution, giving the product (P).

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We start the kinetic analysis with Eq. 9.12, and substitute for $[RH^+]$ using Eq. 9.13. Eq. 9.14 gives the kinetic expression for the mechanism of Eq. 9.11, assuming that the equilibrium between R and RH^+ is completely established. The kinetic expression contains $[H_3O^+]$, as the definition of specific-acid catalysis implies. Hence, the reaction rate depends upon the pH. The expression also contains the acid dissociation constant (K_{aRH^+}) of RH^+ , which is an important factor that we will return to below. Note that k , $[H_3O^+]$, and K_{aRH^+} are constants during the reaction. Hence, we create a new rate constant, k_{obs} , showing that the reaction appears first order (Eq. 9.15, where $k_{obs} = k[H_3O^+]/K_{aRH^+}$).



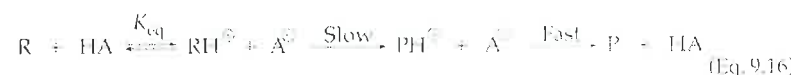
$$\frac{d[P]}{dt} = k[RH^+] \quad (\text{Eq. 9.12})$$

$$[RH^+] = \frac{[H_3O^+][R]}{K_{aRH^+}} \quad (\text{Eq. 9.13})$$

$$\frac{d[P]}{dt} = \frac{k[R][H_3O^+]}{K_{aRH^+}} \quad (\text{Eq. 9.14})$$

$$\frac{d[P]}{dt} = k_{obs}[R] \quad (\text{Eq. 9.15})$$

Let's now examine the same reaction but under conditions for which it is not quite so obvious whether the reaction is catalyzed by the specific acid. If we add an acid such as acetic acid to water, small amounts of hydronium ion are produced, but the acid in highest concentration is acetic acid. Eq. 9.16 shows a mechanism in which the added acid protonates the reactant in an equilibrium prior to the rate-determining step. We designate the acid as HA with the implication that it could be acetic acid performing the protonation. If it were H_3O^+ performing the protonation, we would simply have the same scenario as presented in Eqs. 9.14 and 9.15.



Eq. 9.17 is the starting point for solving the kinetic analysis. The $[RH^+]$ can be derived from the expression for K_{eq} (Eq. 9.18) as shown in Eq. 9.19. However, Eq. 9.19 can be simplified by recognizing that $[HA]/[A^-]$ is equal to $[H_3O^+]/K_{aHA}$, leading to Eq. 9.20. Finally, K_{eq}/K_{aHA} is $1/K_{aRH^+}$ via Eq. 9.18. Hence, we end up with Eq. 9.21. This is exactly the same as Eq. 9.14, which we found for the mechanism shown in Eq. 9.11!

$$\frac{d[P]}{dt} = k[RH^+] \quad (\text{Eq. 9.17})$$

$$K_{eq} = \frac{[RH^+][A^-]}{[R][HA]} = \frac{K_{aHA}}{K_{aRH^+}} \quad (\text{Eq. 9.18})$$

$$[RH^+] = \frac{K_{eq}[HA][R]}{[A^-]} \quad (\text{Eq. 9.19})$$

$$\frac{d[P]}{dt} = \frac{kK_{eq}[R][H_3O^+]}{K_{aHA}} \quad (\text{Eq. 9.20})$$

(5)

$$\frac{d[P]}{dt} = \frac{k[R][H_3O^+]}{K_{aRH}} \quad (\text{Eq. 9.21})$$

This derivation teaches an important lesson. If the acid catalyst is involved in an equilibrium prior to the rate-determining step, and it is not involved in the rate-determining step, then the kinetics of the reaction will depend solely upon the concentration of the specific acid. This is true even if an added acid (such as acetic acid) is involved in protonating the reactant. The reason for this is that when a prior equilibrium is established, the concentration of RH^+ determines the rate of the reaction (Eqs. 9.12 and 9.17). The concentration of RH^+ depends solely upon the pH and the pK_a of RH^+ , and does not depend upon the concentration of the acid HA that was added to solution.

A similar kinetic expression can be derived for the use of a catalytic base, B . When B is involved in an equilibrium with a reactant (RH) prior to a rate-determining step, Eqs. 9.22, 9.23, and 9.24 describe the situation (see Exercise 2). Now K_a and $[H_3O^+]$ trade places in the numerator and denominator relative to the acid-catalyzed scenario (Eq. 9.21). The same expression will be derived if either the specific base or an added base is used in the equilibrium. Once again, because $[R^-]$ controls the rate of the reaction, it is the pH of the solution and the pK_a of RH that are important, not the amount of B present in the solution. Finally, recognizing that $kK_{aRH}/[H_3O^+]$ is a constant during the reaction gives a kinetic expression that is first order in $[RH]$ only (Eq. 9.25, where $k_{\text{obs}} = kK_{aRH}/[H_3O^+]$).



$$\frac{d[PH]}{dt} = k[R^-] \quad (\text{Eq. 9.23})$$

$$\frac{d[PH]}{dt} = \frac{kK_{aRH}[RH]}{[H_3O^+]} \quad (\text{Eq. 9.24})$$

$$\frac{d[PH]}{dt} = k_{\text{obs}}[RH] \quad (\text{Eq. 9.25})$$

The analysis given above did not show any particular reaction, because we wanted to develop the mathematics in a general fashion. To get a better feeling for specific catalysis, we show possible mechanisms for the hydration of a carbonyl using specific-acid and specific-base catalysis in Figure 9.6. Note in each case the equilibrium involving the acid or base is prior to the rate-determining step. It is important to note that we have designated the second step in Figure 9.6 B as rate-determining solely for discussion purposes, so that the mechanism corresponds to the definition of specific-base catalysis. In reality, nucleophilic attack by hydroxide would be rate-determining, because equilibria involving solely proton transfers are often established at diffusion controlled rates (see further discussion of this figure on page 512).

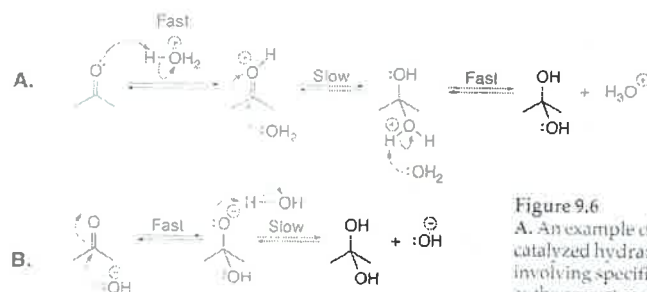


Figure 9.6

A. An example of a possible mechanism involving acid-catalyzed hydration of acetone. B. An example of involving specific-base-catalyzed hydration. Do as the correct mechanisms for these addition reactions, instead, as simply possibilities highlighting them. Certainly, the order of relative rates in part B would

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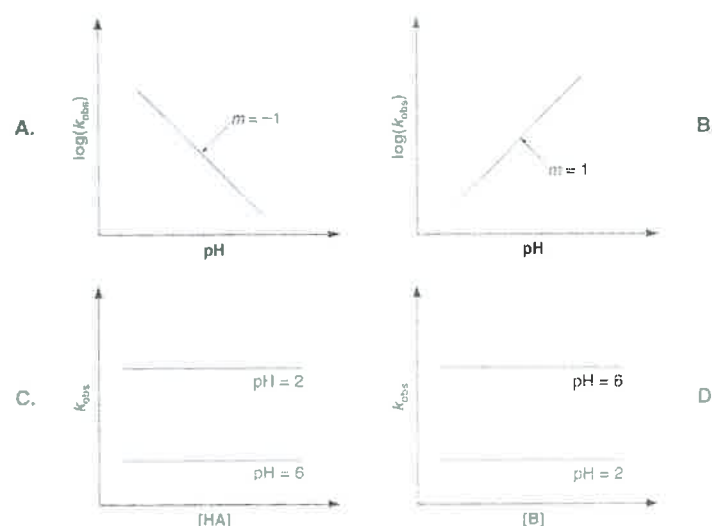


Figure 9.7

The distinctive kinetic plots for specific-acid and specific-base catalysis. A. The pH dependence of $\log(k_{\text{obs}})$ for a specific-acid-catalyzed reaction. B. The pH dependence of $\log(k_{\text{obs}})$ for a specific-base-catalyzed reaction. C. The dependence of k_{obs} for a specific-acid-catalyzed reaction on the concentration of an added acid HA at constant pH. D. The dependence of k_{obs} for a specific-base-catalyzed reaction on the concentration of an added base B at constant pH. The pH values 2 and 6 are just chosen as examples and are not indicative of any particular scenario.

Kinetic Plots

The hallmark of specific-acid or specific-base catalysis is that the rate depends upon the pH and not upon the concentration of various acids or bases. This always means that an equilibrium involving the acid or base occurs prior to the rate-determining step, and the acid or base is not involved in the rate-determining step itself. Experimentally, such reactions produce very distinctive kinetic plots. A plot of pH vs. the $\log(k_{\text{obs}})$ values produces a straight line whose slope is -1 for acid catalysis or 1 for base catalysis (Figures 9.7 A and B). The slopes of ± 1 result because each one-unit change in pH changes the concentration of $[H_3O^+]$ or $[HO^-]$ by a factor of 10, and $[H_3O^+]$ or $[HO^-]$ has been incorporated into k_{obs} . Furthermore, if we keep the pH constant, and change the concentration of an added acid HA or base B, there is no change in k_{obs} (Figures 9.7 C and D). Recall that one can change the concentration of an acid HA or base B and keep the pH constant by keeping the ratios of $[HA]/[A^-]$ or $[B]/[BH^+]$ constant, respectively (see the Henderson-Hasselbach equation—Eq. 5.12).

Q6. C. Explain Kinetics vs thermodynamics control of reaction with suitable example.

(3)

The terms kinetic control and thermodynamic control are concerned with the manner in which the ratios of products of a reaction are determined. When a reaction is under kinetic control, the ratio of two or more products is determined by the relative energies of the transition states leading to these products. The relative stabilities of the products do not matter.

Under thermodynamic control, the ratio of the products is determined solely by the relative energies of the products. In this case the energies of the pathways leading to the products do not matter.

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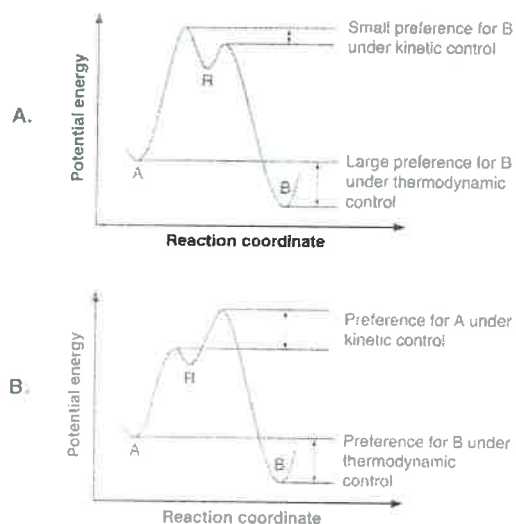


Figure 7.13
Diagrams used to explain kinetic control versus thermodynamic control.
A. The kinetic product and thermodynamic product are both B.
B. The kinetic product is A and the thermodynamic product is B.

Sulfonation of Naphthalene

Reaction that illustrates the concept of kinetic vs. thermodynamic control is the sulphonation of naphthalene with SO_3 in H_2SO_4 .²

When the reaction is run at 80 °C, 1-naphthalenesulfonic acid is the major product; at 160 °C, 2-naphthalenesulfonic acid is the major product.

The intermediates in the sulfonation are arenium ions. The relative energies of the arenium ions should approximate the energies of the transition states leading to the formation of the sulfonic acids.

2-Naphthalenesulfonic acid is more stable than 1-naphthalenesulfonic acid because of an unfavorable steric interaction between the sulfonic acid group in the 1-position and the hydrogen in the 8-position.

The arenium ion leading to 1-naphthalenesulfonic acid is more stable than the arenium ion leading to the 2-isomer because of better resonance stabilization.

Explanation 1½ marks and example 1½ marks

(only)

4

