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Physical Chemistry

1. Describe how variation method and perturbation method dealing with the time-independent Schroedinger equation for systems of several interacting particles.(15%)

2. Describe the procedure of Hartree-Fock calculation.(15%)

3. Does the solubility of a solid in a liquid exhibit appreciable pressure dependence?(10%)

4. Describe how conventional transition-state theory dealing with the reaction rate calculation.(10%)

無機化學 (50分)

1. Draw the crystal field splitting diagrams of d-orbitals for (i) an octahedral complex ML_6 (ii) a square planar complex ML_4, and (iii) a linear complex ML_2. (9%)

2. Compounds that have the same chemical formula but different structural arrangement are called isomers. Briefly describe the (i) linkage isomerism, (ii) optical isomerism, and (c) stereo isomerism by using the idealized complex $Co(Cl)_2(Br)_2(SO_2)(H)$. (9%)

3. Draw a correct structure for each of the following compounds: (12%)

   (i) $(\eta^5-C_5H_5)_2Ni$　　(ii) Al_2Me_6　　(iii) $Fe(CO)_5$　　(iv) O_3

4. Give the products for each of the following reactions: (12%)

   (i) $CaCO_3 \xrightarrow{\triangle}$

   (ii) $W(CO)_4(NCMe)_2$ + $(Me)_2PCH_2CH_2P(Me)_2 \longrightarrow$

   (iii) $2\,Na^+C_5H_4^-$ + $FeCl_2 \longrightarrow$

   (iv) $Cu(H_2O)_6^{2+}(aq)$ + excess $NH_3(aq) \longrightarrow$

5. Describe the following terms: (8%)

   (i) chemical vapor deposition of metal film

   (ii) nonlinear optics metal-containing materials

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ANALYTICAL CHEMISTRY

Note: Always consider the significant figures in all your calculations!!

(7%) 1.(a) For a solution that is 0.0100 M in KCl, calculate the concentration of K^+ in ppb. (K= 39.10, KCl= 74.45)

(b) What does "ppb" stand for ?

(c) 0.821 + 1.73 - 2.0843 = ?

(7%) 2. Calculate the pH of a solution prepared by mixing 50.00 mL of 0.0800 M NaH_2PO_4 with 40.00 mL of 0.0400 M HCl. (for H_3PO_4: $K_1 = 7.11 \times 10^{-3}$; $K_2 = 6.34 \times 10^{-8}$; $K_3 = 4.2 \times 10^{-13}$; also, P = 31.0 ; Na = 23.0)

(7%) 3. Calibration curve method and standard addition method are two common techniques for quantitative analysis of unknown samples.

(a) What is/are the difference(s) between them?

(b) Which method is usually better? Why?

(8%) 4. Monochromator is a very important component of various spectrophotometers, e.g.. UV/Vis. IR. AA,...etc.

(a) What is the monochromator?

(b) Show the schematic diagram of a Czerney-Turner monochromator and explain how it works.

(7%) 5. FID is a common detector for GC.

(a) What does FID stand for (in English)?

(b) Show the schematic diagram of FID and explain how it works.

(c) What are the advantage(s) and disadvantage(s) of this detector? Why?

(7%) 6.(a) What is the reversed-phase liquid chromatography (LC)?

(b) Predict the elution order of n-pentane, n-pentanol, and n-hexanol in a reversed-phase LC. Why?

(7%) 7. Cyclic voltammetry (CV) is used principally to characterize the redox properties of compounds and to study the mechanism of redox reactions.

(a) Show the potential waveform used in CV.

(b) If a typical cyclic voltammogram (CVgram) is shown in Fig. 1, what information can you obtain from this CVgram ?
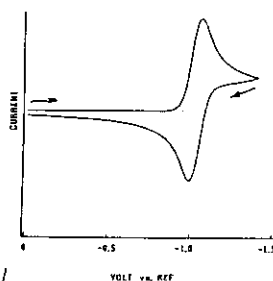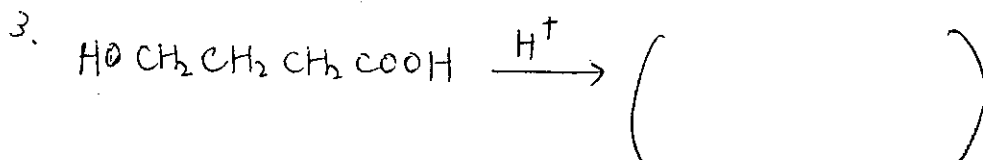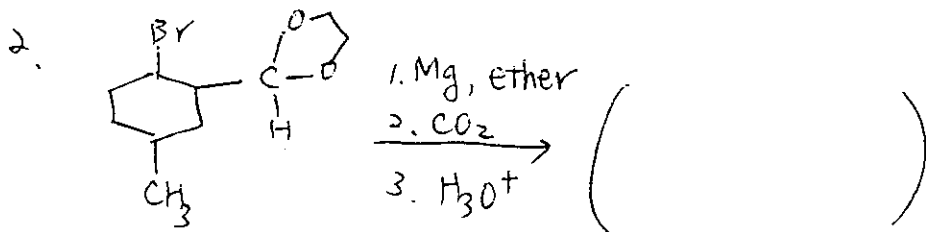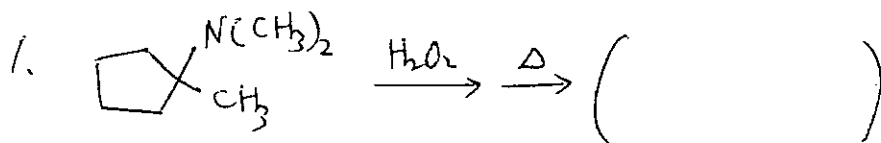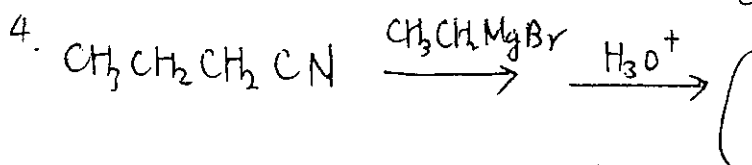

Fig. 1　　　VOLT vs. REF

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ORGANIC CHEMISTRY

一. Give the major product of the following reactions. (3% each)

1. $\xrightarrow{H_2O_2}$ $\xrightarrow{\Delta}$ (　　　　　　)

2. $\xrightarrow[\text{3. } H_3O^+]{\substack{\text{1. Mg, ether}\\ \text{2. } CO_2}}$ (　　　　　　)

3. $HOCH_2CH_2CH_2COOH \xrightarrow{H^+}$ (　　　　　　)

   hint: this is a cyclic adduct

4. $CH_3CH_2CH_2CN \xrightarrow{CH_3CH_2MgBr} \xrightarrow{H_3O^+}$ (

   hint: the product is a ketone
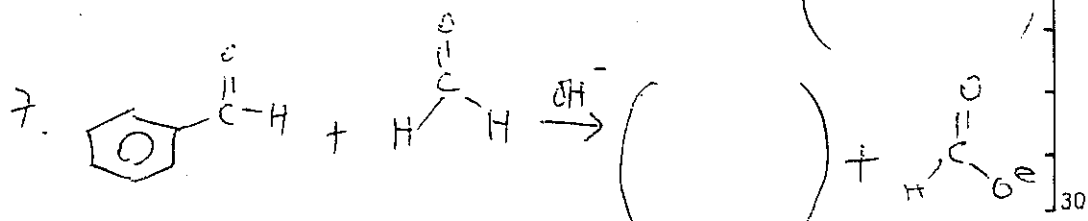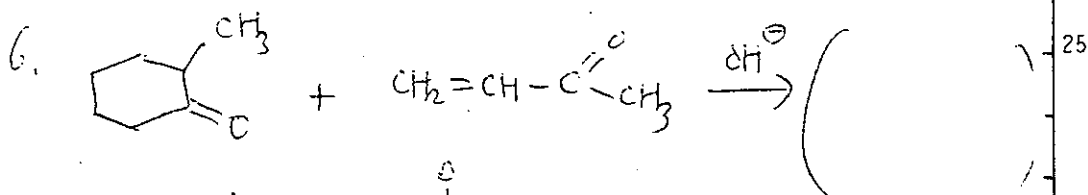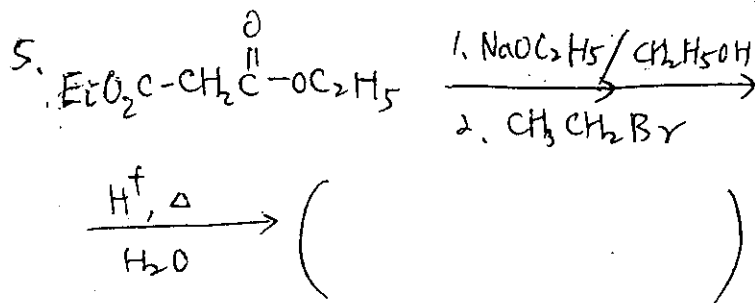
5. $EtO_2C-CH_2\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaOC_2H_5 / CH_2H_5OH}$

   $\xrightarrow[H_2O]{H^+, \Delta}$ (　　　　　　)

6. $+$ $CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow{\overset{\ominus}{OH}}$ (

7. $\overset{\overset{O}{\|}}{C}-H$ $+$ $H-\overset{\overset{O}{\|}}{C}-H$ $\xrightarrow{OH^-}$ (　　) $+$

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8. [benzene] + CH₃-C(=CH₂)-CH₃ $\xrightarrow{H^+}$ (   )   (   )

9. [benzene] + CH₃CH₂-C(=C)-Cl $\xrightarrow{AlCl_3}$

$\xrightarrow[aq. HCl]{Zn(Hg)}$ (   )   (   )

10. [fused ring structure] $\xrightarrow{Br_2}$ (   )

hint: this product is a dibromo compound
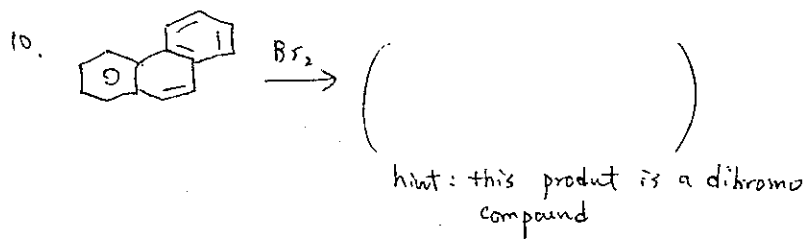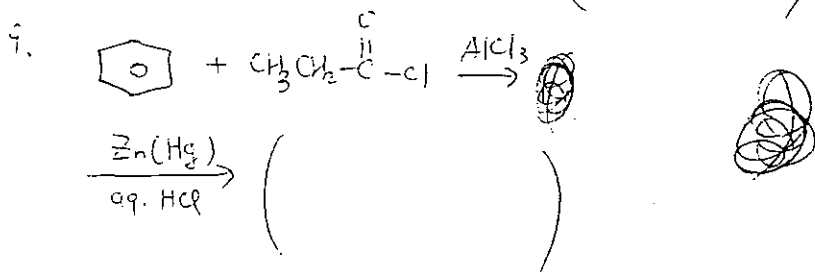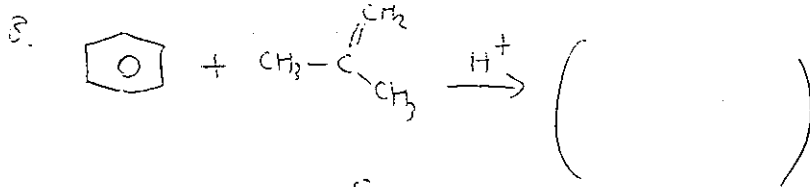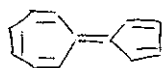
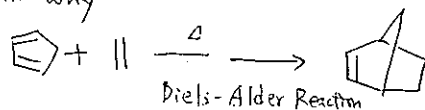二. Explain the following problems briefly (5% each)

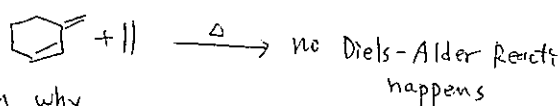1. Why pyrrole is a much weaker base than pyridine.

pyrrole   pyridine
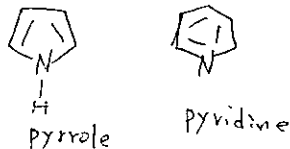
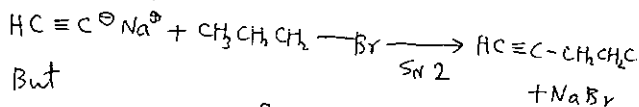2. The following hydrocarbon has an unusually large dipole moment. Why?

3. Explain why

[cyclopentadiene] + || $\xrightarrow{\Delta}$ [bicyclic product]   Diels-Alder Reaction

But

[methylenecyclopentene] + || $\xrightarrow{\Delta}$ no Diels-Alder Reacti happens

4. Explain why

$HC \equiv C^{\ominus} Na^{\oplus} + CH_3CH_2CH_2-Br \xrightarrow{S_N2} HC \equiv C-CH_2CH_2C + NaBr$

But

$CH_3CH_2C \equiv C^{\ominus}Na^{\oplus} + H_3C-CH(Br)-CH_3 \xrightarrow{E_2} CH_3CH_2-C \equiv C-H + H_2C=CH-CH_3 + Br^{\ominus}$

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