國立中山大學九十三學年度碩士班招生考試試題

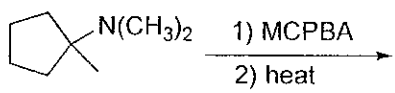
科目：有機化學【化學系碩士班】

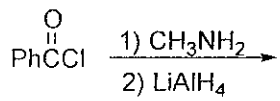
1. Define each term and give an example. (20 pts.)

   (a) Azide (b) Crown ether (c) Heterocyclic compound

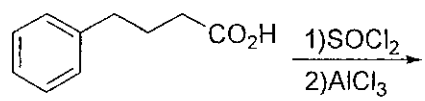
   (d) The endo rule of Diels-Alder reactions (e) Polygon rule

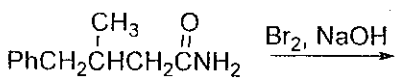
2. predict the major products (including stereochemistry) of the following reactions. (45 pts.)

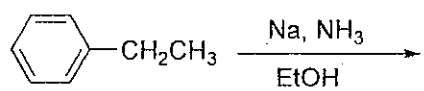
(a) 

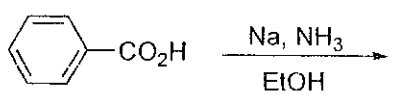
(b) 

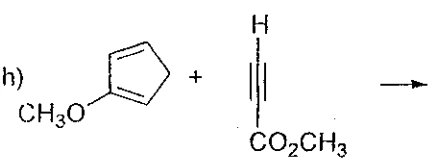
(c) 1-bromopentane $\xrightarrow[2)LiAlH_4]{1)\ NaN_3}$

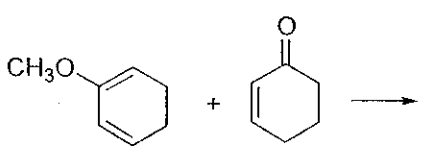
(d) 

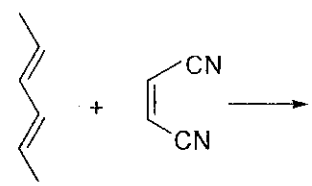
(e) 

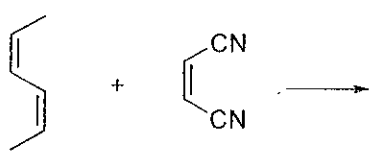
(f) 

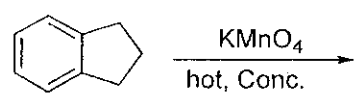
(g) 

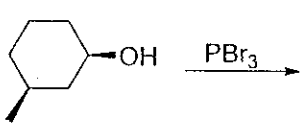
(h) 

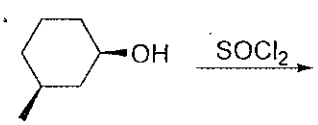
(i) 

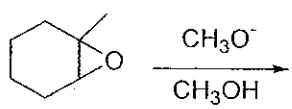
(j) 

(k) 

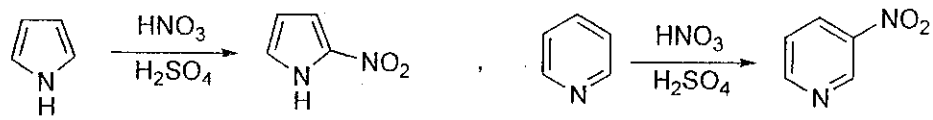
(l) 

(m) 

(n) 

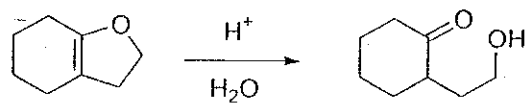
(o) 

3. Explain why nitration of pyrrole occur only at the 2-position whereas nitration of pyridine occur at the 3-position. (10 pts)

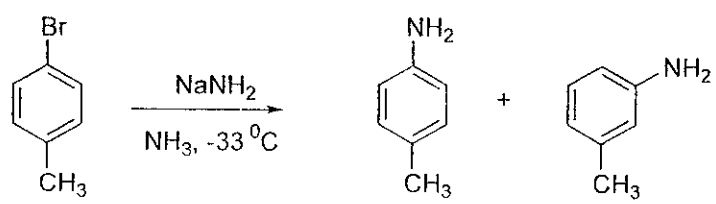


4. Give mechanisms for the following reactions. (10 pts.)

(a)



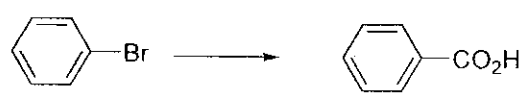
(b)



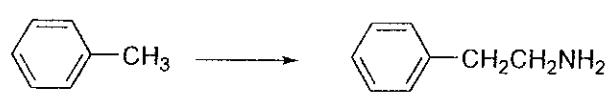
(50%) (50%)

5. Accomplish the following syntheses. (you may use any necessary reagents). (15 pts.)

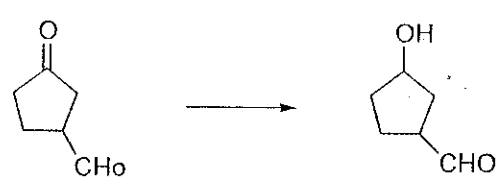
(a)



(b)



(c)



Inorganic Chemistry

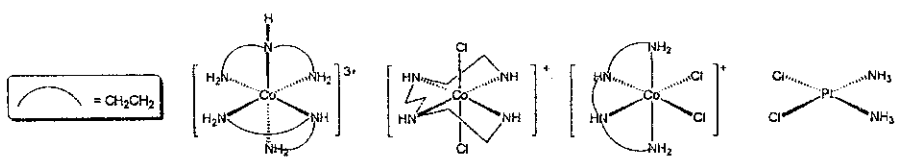
Questions 1-3: Atomic structure and the periodic table

1. (6 points) Give the symbols for each element in *group 4* (recommended by IUPAC).
2. (5 points) We usually expect the atomic radius to increase down a group in the periodic table. The atomic radii for group 4 elements are 1.477 Å, 1.593 Å, and 1.476 Å, respectively, following the order of increasing atomic number. Suggest why the atomic radius of the group 4 elements breaks the rule.
3. (5 points) Give the effective nuclear charge on a 3d electron in the lightest member of the group 4 elements.

Questions 4-6: Transition metal complex

4. (9 points) Determine the number of unpaired electrons, spin-only magnetic moment (in the unit of Bohr magneton), and ligand field stabilization energy (in the unit of Δ_o or Δ_t) for $[Cr(CN)_6]^{4-}$.
5. (6 points) Give the Mulliken symbols for the HOMO and LUMO of $[Cr(CN)_6]^{4-}$.
6. (5 points) Does $[Cr(CN)_6]^{4-}$ exhibit Jahn-Teller effect? Explain briefly.

Questions 7-10: Stereochemistry



7. (5 points) Determine the chirality label(s) (Δ, Λ, δ, λ, α, β, cis, trans, etc.) for compound A.
8. (5 points) Determine the chirality label(s) (Δ, Λ, δ, λ, α, β, cis, trans, etc.) for compound B.
9. (5 points) Determine the chirality label(s) (Δ, Λ, δ, λ, α, β, cis, trans, etc.) for compound C.
10. (5 points) Determine the chirality label(s) (Δ, Λ, δ, λ, α, β, cis, trans, etc.) for compound D.

Questions 11-12: Spectroscopy

11. (10 points) Explain the trend found in the IR spectroscopic data for CO stretching bands of *fac*-$Mo(CO)_3(PF_3)_3$ (2090 and 2055 cm^{-1}), *fac*-$Mo(CO)_3(PCl_3)_3$ (2040 and 1991 cm^{-1}), and *fac*-$Mo(CO)_3(PMe_3)_3$ (1945 and 1854 cm^{-1}).
12. (10 points) The coupling constant $^1J_{CH}$ of 122 Hz is usually found for a normal sp^3-hybridized carbon atom in the NMR spectroscopy. Explain why the CH_2 moiety in $M(\eta^3\text{-}CH_2C_6H_5)$ exhibits $^1J_{CH}$ of 152 Hz, where M is a transition metal.

Questions 13-15: Group theory

13. (4 points) Illustrate the *perspective* structures for the two possible isomers of $FeCl_2(CO)_4$.
14. (10 points) Determine the number of IR-active C-O stretching vibrations for C_{2v}-symmetric $FeCl_2(CO)_4$. Indicate the Mulliken symbols for these vibration modes.
15. (10 points) Determine the number of Raman-active C-O stretching vibrations for D_{4h}-symmetric $FeCl_2(CO)_4$. Indicate the Mulliken symbols for these vibration modes.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

物理化學 Physical Chemistry

1. (10%) What are the units, if any, for the wave function of a particle in a one-dimensional box?

2. (10%) Why does $\psi^* \psi$ have to be everywhere real, nonnegative, finite, and of definite value?

3. (10%) For an isolated hydrogen atom, why must the angular momentum vector L lie on a cone that is symmetric about the z-axis? Can the angular momentum operator ever point exactly along the z-axis?

4. (12%) The spacing between the lines in the microwave spectrum of $H^{35}Cl$ is 6.350×10^{11} Hz. Calculate the bond length of $H^{35}Cl$. $h = 6.626 * 10^{-34} * J * s$,

5. (12%) A one-mole sample of $CO_2(g)$ occupies 2.00 dm^3 at a temperature of 300 K. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is 0.750 dm^3, calculate the smallest value P_{ext} can have, assuming that $CO_2(g)$ satisfies the van der Waals equation of state under these conditions. Calculate the work involved using this value of P_{ext}. For CO_2, $a = 3.6551 dm^6 * bar * mol^{-2}$, $b = 0.042816 dm^3 * mole^{-1}$

6. (12%) Use the following data for methanol at one atm to plot $\overline{G}$ versus T around the normal boiling point (337.668 K). What is the value of $\Delta_{vap}\overline{H}$?

T/K	$\overline{H}$/kJ·mol^{-1}	$\overline{S}$/J·mol^{-1}·K^{-1}
240	4.7183	112.259
280	7.7071	123.870
300	9.3082	129.375
320	10.9933	134.756
330	11.8671	137.412
337	12.5509	139.437
337	47.8100	243.856
350	48.5113	245.937
360	49.0631	247.492
380	50.1458	250.419
400	51.2257	253.189

7. (12%) The value of $\Delta_r H^\circ$ is 34.78 kJ·mol^{-1} at 1000 K for the reaction described by

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Given that the value of K_p is 0.236 at 800 K, estimate the value of K_p at 1200 K, assuming that $\Delta_r H^\circ$ is independent of temperature.

8. (10%) Consider the reaction mechanism

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \qquad (1)$$

$$C \xrightarrow{k_2} P \qquad (2)$$

Write the expression for $d[P]/dt$, the rate of product formation. Assume equilibrium is established in the first reaction before any appreciable amount of product is formed.

9. (12%) Calculate the hard-sphere collision theory rate constant for the reaction

$$NO(g) + Cl_2(g) \Longrightarrow NOCl(g) + Cl(g)$$

at 300 K. The collision diameters of NO and Cl_2 are 370 pm and 540 pm, respectively. The Arrhenius parameters for the reaction are $A = 3.981 \times 10^8$ dm^3·mol^{-1}·s^{-1} and E_a = 84.9 kJ·mol^{-1}. Calculate the ratio of the hard-sphere collision theory rate constant to the experimental rate constant at 300 K.
Assume $k_{thero} = (1000 dm^3 * m^{-3}) * N_A * \sigma_{AB} * <u_r>$, σ_{AB} is the hard sphere collision cross section of A and B, $<u_r>$ is the average relative speed of a colliding pair.

(12%)1.The following devices are commonly used in Quantitative Analysis Laboratory. (1) Show the schematic diagram of each device and (2) briefly describe the purpose to have each device in Quantitative Analysis Laboratory.

(a) buret (b) transfer pipet (c) volumetric flask (d) desiccator

(12%)2. (1) 2.00 ppb Ca^{2+} = ? M Ca^{2+} (Ca = 40.0)

(2) Iron from a dietary supplement tablet can be measured by dissolving it and then converting the iron into solid Fe_2O_3. If the final mass of Fe_2O_3 isolated at the end of experiment was 0.277 g, what is the average mass of iron per dietary tablet? (Fe = 55.85)

(3) Balance and complete the following reaction equation:

$$H_2C_2O_4 + MnO_4^- \rightarrow CO_2 + Mn^{2+}$$

(10%)3. A titration curve for the titration of 25.00 mL of 0.1000 M maleic acid, H_2M, with 0.1000 M NaOH is shown in Fig. 1.

(1) Find pKa1 and pKa2 of H_2M from Fig. 1 and explain why.

(2) Show the first derivative and the second derivative plots of the titration curve in Fig. 1, respectively.

(30%)4. Define the following terms:

(1) faradaic current (2) electroosmotic flow (3) Fourier transform

(4) FID (5) monochromator (6) ensemble averaging

(6%)5. An operational amplifier based circuit, i.e., current-to-voltage converter, is often applied to the measurement of a small photocurrent. Show the circuit of that I/V converter and the corresponding equation about V_{out} and I_{in}.

(10%)6. Scanning probe microscopes (SPMs) are capable of resolving details of surfaces down to the atomic level. One type of SPMs is AFM that is currently the most widely used. (1) What does AFM stand for (in English)? (2) Show the schematic diagram of AFM and explain how it works (including principle, advantage, disadvantage, etc.).

(10%)7. Capillary gas chromatography / mass spectrometry (GC/MS) is a very powerful analytical instrument. (1) What information can you obtain from GC/MS? (2) Show the schematic diagram of a GC/MS.

(10%)8. Atomic absorption spectrometry (AAS) has been the most widely used method for the determination of single elements in analytical samples for nearly half a century. However, two types of interferences, i.e., spectral interference and chemical interference, are still the problems need to be solved. (1) What are spectral interference and chemical interference? Give one example for each type of interference. (2) Name (in English) a radiation source and a detector (or transducer) commonly used in AAS.

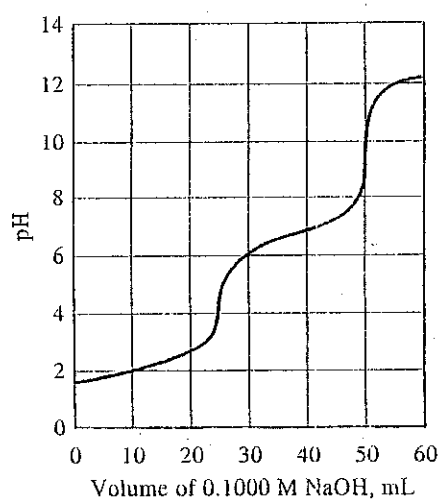


Figure 1