94 學年度 化 學 系（所） 化學、應用化學 組碩士班研究生招生考試
科目_無機化學及有機化學_科號_0602, 0702_共__7___頁第__1_頁 *請在試卷【答案卷】內作答

1. Draw a molecular orbital (M. O.) energy diagram for molecular oxygen (O_2). Label all atomic and molecular orbitals. Show which atomic orbitals give rise to which molecular orbitals. Based on your M. O. diagram, calculate the bond order and determine the magnetic property of O_2. (8%)

2. How do the light absorption and emission bands of semiconductor quantum dots shift compared to their bulk counterparts? Why? One may consider the particle in a box situation. (3%)

3. a) Give the crystal field diagram for the tetrahedral complex ion $CoCl_4^{2-}$. Label all orbitals. b) The complex ion $PdCl_4^{2-}$ is diamagnetic. Propose a structure for $PdCl_4^{2-}$ and explain why. (6%)

4. a) How many atoms are there in the unit cell of silver with a face-centered cubic (fcc) structure. b) How many equivalent nearest neighbors are there for silver in the fcc structure? c) Why is silver a metal whereas silicon is a semiconductor? d) How would the electrical conductivity of a semiconductor behave with increasing temperature? (5%)

5. a) Balance the following oxidation-reduction reaction by using the oxidation states method. $Cu(s) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$ b) According to the above equation, which metal has a higher standard reduction potential? c) Would ΔG° for this reaction be positive or negative? (3%)

6. Determine the point group for the following compounds: (5%)
   (1) B_2H_6
   (2) $[Re_2Cl_8]^{2-}$
   (3) The staggered ferrocene
   (4) SF_5Cl
   (5) BIClF

7. For each of the following pairs indicate which substance is expected to be (5%)
   (A) More ionic
   (1) NaCl or CuCl (similar radii) (2) $TiCl_3$ or $TiCl_4$
   (B) More covalent (Fajan's rule)
   (1) $MgCl_2$ or $BeCl_2$ (2) $TiCl_3$ or $TiCl_4$

(C) Harder

(1) Al_2O_3 or Ga_2O_3

8. Both ^{63}Cu and ^{31}P have $I = 1/2$. When CuI is dissolved in $P(OMe)_3$, the ^{63}Cu NMR spectrum shows a five-line pattern with relative intensities 1 : 4 : 6: 4 : 1. What inference can be made about the environment of Cu in this solution? (5%)

9. Select the best answer for the followings: (5%)

(a) Thermally most stable: PH_4Cl PH_4Br PH_4I

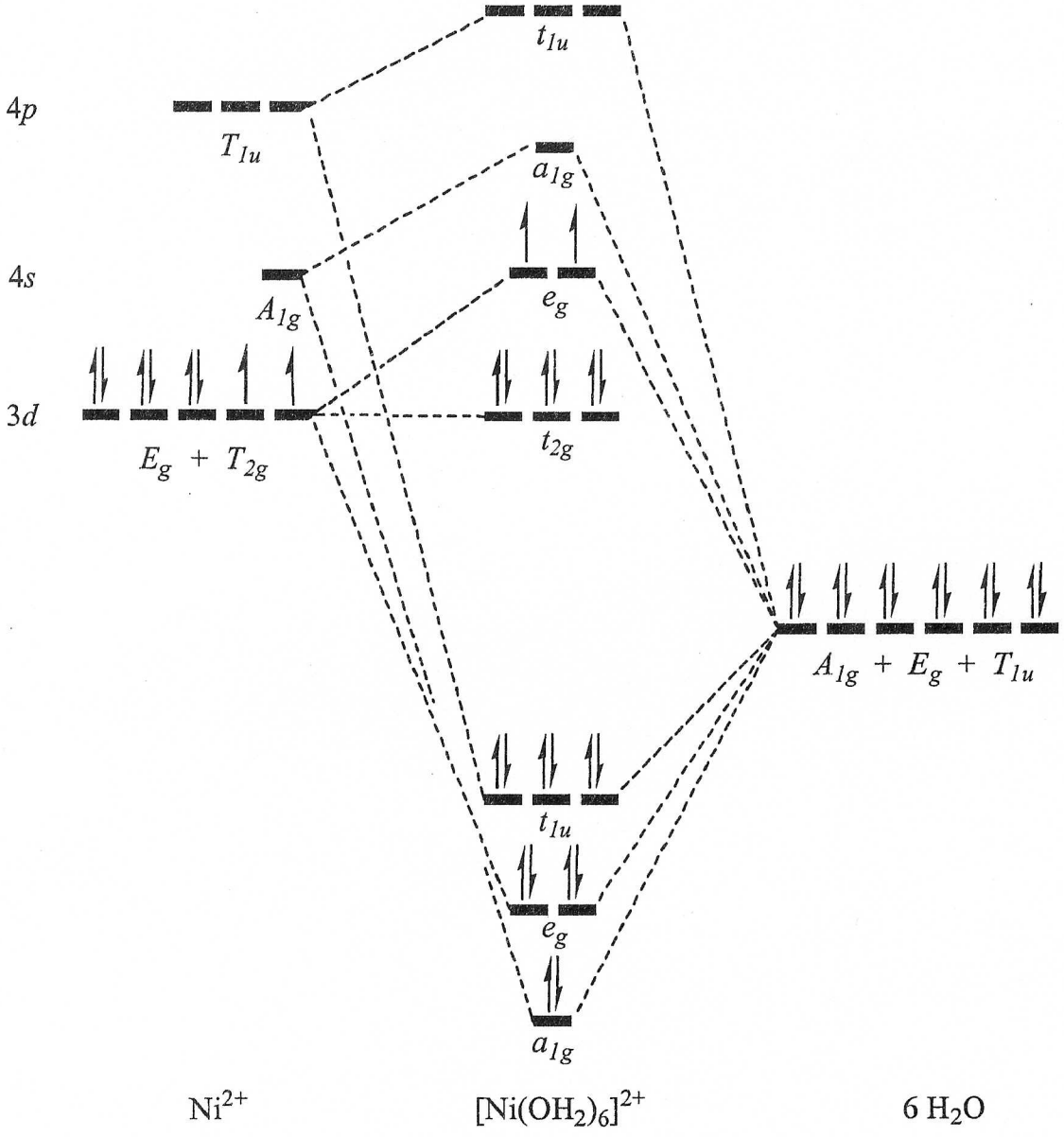
(b) Strongest acid: H_2O H_2S H_2Se H_2Te

(c) Acidic oxide: Ag_2O V_2O_5 CO Ce_2O_3

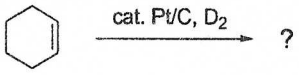
(d) Strongest acid: MgF_2 $MgCl_2$ $MgBr_2$

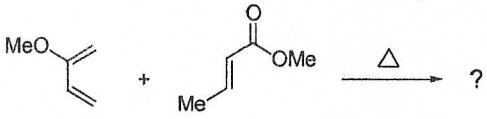
(e) Stronger base (toward a proton): PH_2^- NH_2^-

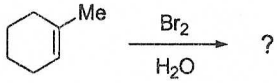
10. For the qualitative MO diagram (without π bonding) for $[Ni(OH_2)_6]^{2+}$ as shown on page 3: (a) Identify the portion of the diagram considered by Crystal Field Theory. (b) Designate the portion of the diagram considered by Valence Bond Theory. (c) Sketch the π-bonding effect on the magnitude of Δ_o (or 10 Dq). (H_2O is considered as a π-donor ligand.) (5%)

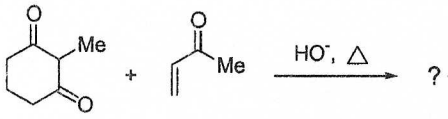

4p
4s
3d
t_{1u}
T_{1u}
a_{1g}
e_g
A_{1g}
t_{2g}
$E_g + T_{2g}$
$A_{1g} + E_g + T_{1u}$
t_{1u}
e_g
a_{1g}
Ni^{2+}
$[Ni(OH_2)_6]^{2+}$
$6\ H_2O$

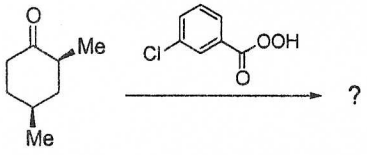
11. Predict the structure of the major product with appropriate stereochemistry, if necessary, for each of the following reactions. (10 %)

(a) 

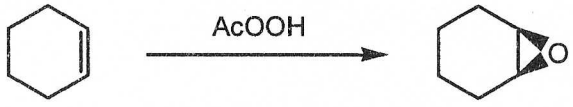
(b) 

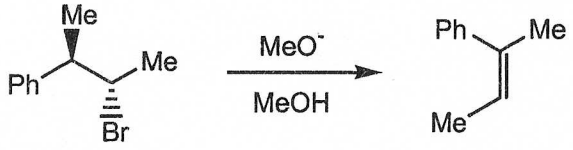
(c) 

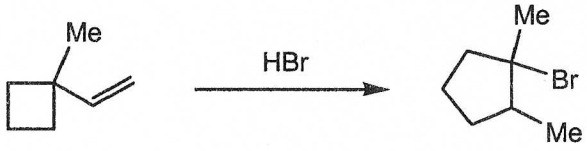
(d) 

(e) 

12. Propose a stepped mechanism for each of the following transformations. (9%)

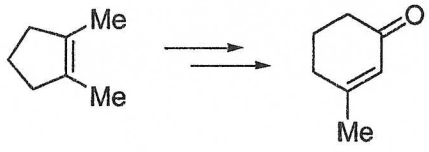
(a) 

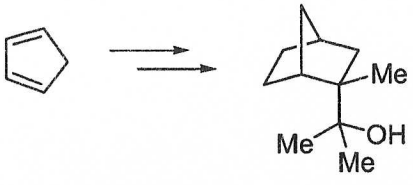
(b) 

(c) 

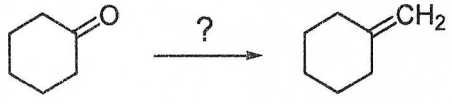
13. Provide a synthetic scheme for each of the following compounds from the readily available starting materials. (12%)

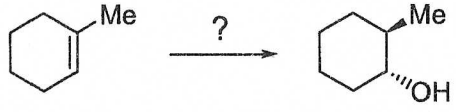
(a) 

(b) 

(c) 

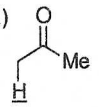
14. Suggest reagents for each of the following transformations. (6%)

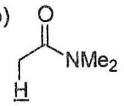
(a) 

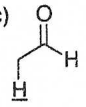
(b) 

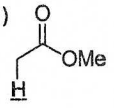
(c) 

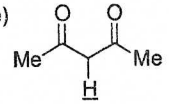
15. Arrange the following compounds in an order of increasing acidity and give a brief explanation of your arrangement. (4%)

(a) 

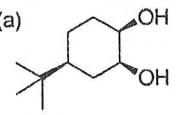
(b) 

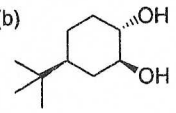
(c) 

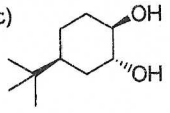
(d) 

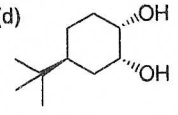
(e) 

16. Which of the following compounds can not be cleaved by HIO_4, and why? (4%)

(a) 

(b) 

(c) 

(d) 

17. Deduce the molecular structure of compound that consists with the spectral data shown on page 7. (5%)

. This compound has the formula $C_9H_{10}O_2$.