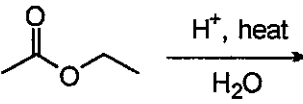


有機化學共 50 分

簡答題（每一題組 5 分，共 50 分，請於『非選擇題作答區』內作答。）

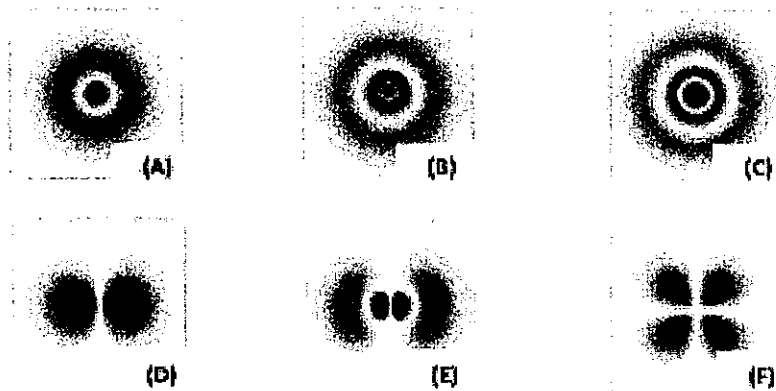
- (1) (a) Give the **structural criteria** for a molecule to be qualified as an **aromatic** compound.  
(b) Give a specific **molecular structure** that is potentially **anti-aromatic**.
- (2) (a) Give the **structural criteria** for a substrate to be qualified to undergo an **E2** reaction.  
(b) In addition to item (a), what is the required **reaction condition** to proceed an E2 reaction?
- (3) (a) Give the molecular structures of **Acetone, Chloroform, Acetonitrile, and Toluene**.  
(b) Rank the relative **polarity** of molecules in item (a).
- (4) (a) Give the molecular structure of the **enolate ion of Pentane-2,4-dione**, also called acetylacetonate.  
(b) Draw all the possible **resonance structures** of the species in item (a).
- (5) (a) Define the term **Electrophilic Aromatic Substitution (EAS)**.  
(b) Give a specific example of EAS reactions, including substrate, reagent(s), and product.
- (6) (a) Draw the **Newman Projection** of butane in the **Gauche** form.  
(b) Draw the molecular structure of **(2R,3S)-3-Methylpentan-2-ol** and its enantiomer.
- (7) (a) Rank the relative **acidity** of **Cyclohexanol, 4-Nitrophenol, Benzoic acid, and 1-Butanethiol**.  
(b) Which of the compounds in item (a) is relatively **more difficult** to oxidize.
- (8) (a) Predict and draw the  $^1\text{H}$  NMR spectrum (300 MHz) of  **$\text{ClCH}_2\text{COOCH}_2\text{CH}_3$**  in  $\text{CDCl}_3$  at room temperature.  
(b) Predict the **relative peak intensity** of the  $\text{M}^+$ ,  $(\text{M}+1)^+$ , and  $(\text{M}+2)^+$  peaks of the compound in item (a) in a mass spectrum.  
(c) Predict the **carbonyl stretching frequency** (in  $\text{cm}^{-1}$ ) of the compound in item (a).
- (9) (a) Give a specific example of **Diels-Alder** reactions, including substrate, reagent(s), and product.  
(b) Give a specific example of **Wittig** reactions, including substrate, reagent(s), and product.
- (10) (a) Give the products of this reaction:  
  
(b) Write the reaction mechanism of the above reaction in item (a) with curved arrows.

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無機化學 共 50 分

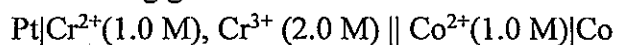
多選題，每題 5 分，共 50 分 ※ 本大題請用 2B 鉛筆作答於答案卡，並先詳閱答案卡上之「畫記說明」。

(1) Which of the following description(s) of the orbital is(are) correct?

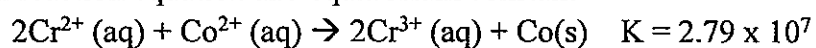


- The angular parts of orbitals A and C are different because they have different principal quantum numbers ( $n = 2 \sim 4$ ).
- Orbital E and F have the same total number of nodes.
- In some atoms, the energy of F is lower than that of C.
- In  $\text{He}^+$ , orbitals B and E have the same energy.
- None of the above.

(2) Considering the following galvanic cell at 25 °C:



Overall reaction equation and equilibrium constant



Which of the following statement(s) is(are) correct?

- The cathode is Co and anode is Pt.
- The standard Gibbs free energy change,  $\Delta G^\circ$ , for the reaction is  $-42.5 \text{ kJ/mol}$ .
- The cell potential ( $E$ ) of this galvanic cell is  $0.220 \text{ V}$ .
- The Gibbs free energy change  $\Delta G$  under the given condition is  $-3.4 \text{ kJ/mol}$ .
- None of the above.

(3) Which of the following description about acids is/are correct?

- $\text{HNO}_3$  behaves as a Brønsted base in liquid  $\text{H}_2\text{SO}_4$ .
- In aqueous solution,  $\text{HI}$  ( $pK_a = -11$ ) is more acidic than  $\text{HCl}$  ( $pK_a = -7$ ).
- $\text{NH}_3$  ( $pK_{ion} = 27$ ) has a larger acid-base discrimination window than water ( $pK_{ion} = 14$ ). Therefore,  $\text{NH}_3$  is a better solvent in determining the acidity difference of acids.
- The acidity of  $\text{HSO}_3\text{F}$  is significantly enhanced upon mixing with  $\text{SbF}_5$  due to the stabilization of the conjugate base.
- None of the above.

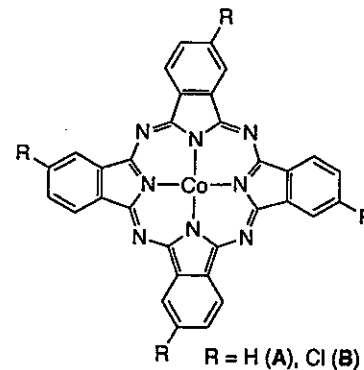
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- (4) If the experimentally determined rate law of the CO substitution reaction of  $\text{Ni}(\text{PR}_3)_4$  is
- $$\text{Ni}(\text{PR}_3)_4 + \text{CO} \rightarrow \text{Ni}(\text{PR}_3)(\text{CO}) + \text{PR}_3$$
- $$\text{rate} = k[\text{Ni}(\text{PR}_3)_4]$$

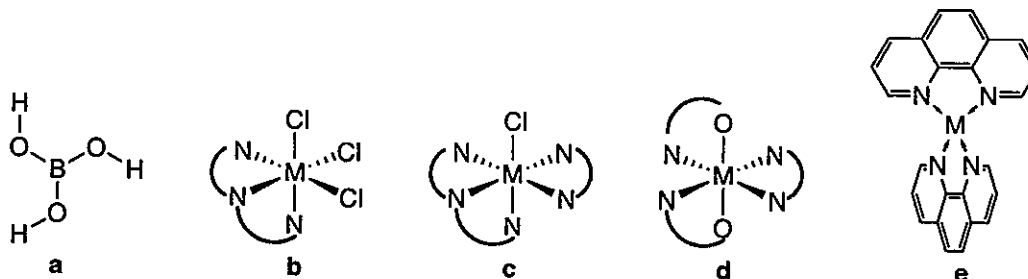
, where  $\text{PR}_3$  is either triethylphosphine ( $\text{PEt}_3$ ) or tri-*tert*-butylphosphine ( $\text{P}(\text{t-Bu})_3$ ), and assuming that the reaction mechanism remains unchanged upon one-electron oxidation or reduction of the complex, which of the following statements is/are correct?

- $\text{Ni}(\text{PR}_3)_4$  features a  $d^8$  metal center and prefers square planar geometry
  - The observed rate law suggests that the reaction proceeds via a dissociative substitution mechanism.
  - The reaction intermediate is  $\text{Ni}(\text{PR}_3)_4(\text{CO})$ .
  - The substitution rate for  $[\text{Ni}(\text{PEt}_3)_4]$  is faster than that of  $\text{Ni}(\text{P}(\text{t-Bu})_3)_4$
  - The reaction rate for  $[\text{Ni}(\text{PR}_3)_4]^+$  is expected to be slower than that of  $\text{Ni}(\text{PR}_3)_4$ .
- (5) Cobalt(II) phthalocyanine and its derivatives are promising electrocatalysts for  $\text{CO}_2$  reduction. The molecular structures of two representative complexes are shown below. Which of the following description(s) is/are correct?

- Phthalocyanine acts as an  $\text{L}_2\text{X}_2$  ligand in the CBC classification.
- The ground-state free-ion term of cobalt(II) is  $^4\text{F}_{3/2}$ .
- The point group of complex B is  $\text{D}_{2d}$ .
- Complex B exhibits a stronger d-d transition than complex A due to the absence of a center of inversion in complex B.
- None of the above.



- (6) The point group and chirality of the following complexes have been assigned. Which assignment(s) is/are correct?



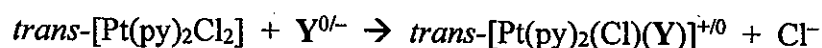
- $\text{D}_{3h}$ , achiral
- $\text{C}_s$ , achiral
- $\text{C}_1$ , chiral,  $\Delta$
- $\text{C}_2$ , chiral,  $\Lambda$
- $\text{C}_{2v}$ , achiral

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- (7) Which of the following statements regarding elementary steps in organometallic reactions is/are correct?
- Migratory insertion combines two ligands into one and therefore reduces the oxidation state of the metal center by one unit.
  - Reductive elimination must occur from coupling two cis-ligands at the metal center.
  - Electron-rich substrates generally undergo oxidative addition more rapidly because they donate more electron density into the empty d orbitals of the metal.
  - $\sigma$ -Bond metathesis is most commonly observed for late transition-metal  $d^8$  complexes.
  - None of the above.

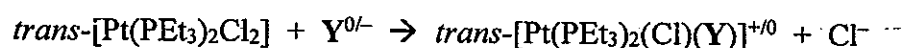
- (8) The ligand substitution rate constants for two  $Pt^{2+}$  complexes are listed below.

**Reaction A:**



$Y^{0/-}$	$k_2 (M^{-1} s^{-1})$
MeOH	$2.7 \times 10^{-7}$
$Cl^-$	$4.5 \times 10^{-4}$
$SCN^-$	$1.8 \times 10^{-1}$

**Reaction B:**



$Y^{0/-}$	$k_2 (M^{-1} s^{-1})$
$Cl^-$	$2.9 \times 10^{-5}$
$SCN^-$	$3.7 \times 10^{-1}$

Which of the following statement(s) is/are correct?

- For reaction A,  $n_{Pt}(Cl^-) = 3.22$  and  $n_{Pt}(SCN^-) = 5.82$
  - If the nucleophilicity discrimination factor ( $s$ ) for reaction A is set to 1, then the  $s$  value for reaction B is 0.78.
  - Based on these data,  $SCN^-$  has a stronger trans effect than  $Cl^-$ .
  - For reaction B, the  $k_2$  value for  $Y = MeOH$  will be smaller than  $2.7 \times 10^{-7}$ .
  - None of the above.
- (9) Which of the following complexes feature(s) a metal-metal bond order  $\geq 2$ ?
- $[Re_2Cl_8]^{2-}$
  - $[Cu_2(OAc)_4]$
  - $[Mo_2(SO_4)_4]^{3-}$
  - $[CpZr(H)_2]_2$
  - None of the above.

- (10) The estimated  $\Delta_o$  and the pairing energies for the metal ions of four complexes are listed below. The estimated  $\Delta_o$  values were calculated using the empirical metal constant  $g$  and ligand factor  $f$  according to  $\Delta_o = g \times f$ .

	Complex	Estimated $\Delta_o$ ( $\text{cm}^{-1}$ ) $\Delta_o = g \times f$	Pairing energy of $M^{n+}$ ( $\text{cm}^{-1}$ )
A	$[\text{Cr}(\text{py})_6]^{2+}$	$14100 \times 1.23$	$\text{Cr}^{2+}$ 23500
B	$[\text{Fe}(\text{CN})_6]^{3-}$	$14000 \times 1.7$	$\text{Fe}^{3+}$ 60,000
C	$[\text{Co}(\text{bpy})_3]^{3+}$	$18200 \times 1.43$	$\text{Co}^{3+}$ 42,000
D	$[\text{CoCl}_6]^{4-}$	$9000 \times 0.78$	$\text{Co}^{2+}$ 19,500

- Among the listed complexes, only complex C is expected to be low-spin.
- The relatively high pairing energies of  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  arise from the +3 charge at the metal center.
- The larger ligand factor  $f$  for  $\text{CN}^-$  (1.7) compared with  $\text{Cl}^-$  (0.78) reflects a stronger nephelauxetic effect of  $\text{CN}^-$ , which increases meta-ligand covalency and therefore enhances the crystal field splitting.
- Replacing  $\text{Fe}^{3+}$  in complex B with  $\text{Os}^{3+}$  would result in a low-spin complex because the more diffuse 5d orbitals of Os increase  $\Delta_o$  and reduce pairing energy.
- None of the above.

試題隨卷繳回