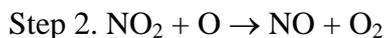


4. (12%) The contribution to the destruction of the ozone layer caused by high-flying aircraft has been attributed to the following mechanism:



- (a) Write the overall reaction. (b) Write the rate law for each step. (c) What is the reaction intermediate? (d) What is the catalyst (if any) in the reaction? (e) How does a catalyst affect the rate of the reverse reaction? (f) How does a catalyst affect ΔH of the reaction?
5. (3% for each question, 18% total) Please write the structural formula (or line structures) of the following molecules. In addition, indicate which of the following molecules are optical isomers and identify the chiral carbon with asterisks (*).
- (a) $CH_3CHBrCH_2Br$
(b) $(CH_3)_2CHCHClC\equiv CH$
(c) $(CH_3CH_2)_2CHCOOCH_3$
(d) 3-methyl-2-pentanol
(e) 2,2-dichlorobutanoic acid
(f) 4,5-dimethyl-3-hexanone
6. (2% for each question, 12% total) Classify each of the following reactions as (1) a free-radical addition reaction, (2) a free-radical substitution reaction, (3) an electrophilic addition reaction, (4) an electrophilic substitution reaction, (5) a nucleophilic substitution reaction, (6) an elimination reaction or (7) a condensation reaction :
- (a) The reaction of bromobenzene with a mixture of HNO_3 and concentrated H_2SO_4
(b) The reaction of 1-butene with Cl_2 in the absence of light
(c) The reaction of 2-methyl-butane with Cl_2 in the presence of UV light
(d) The synthesis of a protein
(e) The reaction of methylamine with butanoic acid
(f) The polymerization of styrene, $CH_2CHC_6H_5$
7. (10%) Please draw the resonance Lewis structure of cyanobenzene (C_6H_5CN) and write the structural formula of the main product of brominating cyanobenzene.

8. (2% for each question, 6% total) Please write the structural formula (or line structure) of the monomers of each of the following polymers for which one repeating unit is shown:

(a)	(b)	(c)
$-(\text{CH}(\text{CH}_3)\text{CH}_2)_n-$	$-(\text{OC}(\text{CH}_3)_2\text{C}=\text{O})_n-$	

9. Consider the complex potassium hexacyanomanganate(II). (2% for each question, 28 % total)
- What is the formula of the complex?
 (a) $\text{K}[\text{Mg}(\text{CN})_6]$ (b) $\text{Po}[\text{Mg}(\text{CN})_5]$ (c) $\text{K}_2[\text{Mn}(\text{CN})_6]$
 (d) $\text{K}_4[\text{Mn}(\text{CN})_6]$ (e) $\text{Po}_4[\text{Mn}(\text{CN})_6]$
 - What is the oxidation number of the metal in hexacyanomanganate(II)?
 (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
 - How many d electrons does the metal in hexacyanomanganate(II) ion have?
 (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
 - How many unpaired d electrons does the metal in hexacyanomanganate(II) ion have?
 (a) 1 (b) 2 (c) 3 (d) 4 (e) 5
 - What is the electron configuration of the metal in hexacyanomanganate(II) ion?
 (a) t_{2g}^5 (b) $t_{2g}^3 e_g^2$ (c) t_{2g}^6 (d) t_{2g}^2 (e) $e^2 t_2^3$
 - Cyanide is a (a) zero-field (b) weak-field (c) strong-field
 (d) magnetic-field (e) oil-field ligand.
 - The complex is a (a) zero spin (b) high spin (c) low spin
 (d) self spin (e) fast spin complex.
 - When two cyanido ligands of hexacyanomanganate(II) ion are replaced by another type of ligand L, the following ones will be formed.
 (a) structural isomers (b) enantiomers (c) linkage isomers
 (d) geometrical isomers (e) optical isomers
 - When two bidentate ligands $\text{L}^{\wedge}\text{L}$ are used to replace cyanido ligands of hexacyanomanganate(II) ion, how many isomers are possible?
 (a) 2 (b) 3 (c) 4 (d) 5 (e) 6

- (10) Which one of the following element is in a group the same as the metal in hexacyanomanganate(II) ion? (a) Ca (b) Ra (c) Te (d) Fe (e) Re
- (11) The geometry of hexacyanomanganate(II) ion is:
(a) tetrahedral (b) square planar (c) pentagonal bipyramidal (d) octahedral
(e) cubic
- (12) Which one of the following ligands can split the d orbitals of hexacyanomanganate(II) ion similar to cyanide?
(a) H₂O (b) I⁻ (c) NH₃ (d) F⁻ (e) CO
- (13) Which ones of the following metal orbitals in hexacyanomanganate(II) ion have the lowest energy?
(a) t_{2g} (3d_{xy}, 3d_{yz}, 3d_{zx}) (b) t_{2g} (3d<sub>x²-y²}, 3d_{z²}}) (c) e_g (3d_{xy}, 3d_{yz}, 3d_{zx})
(d) e_g (3d_{x²-y²}, 3d_{z²}}) (e) 4s}</sub>
- (14) A rich supply of the metal in hexacyanomanganate(II) ion can be found:
(a) in desert (b) in river (c) on ocean floor (d) in air (e) in vegetables

Answers: (滿分為 104 分)

Ans 1: (2% for each answer; 6% total)

- (a) molecule · cm⁻³ · s⁻¹
- (b) s⁻¹
- (c) cm³ · molecule⁻¹ · s⁻¹

Ans 2: (2% for each answer; 6% total)

- (a) bimolecular
- (b) unimolecular
- (c) termolecular (or trimolecular)

Ans 3: (6%)

cat = catalyzed

$$\frac{\text{rate(cat)}}{\text{rate(uncat)}} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = 1000 = \frac{Ae^{-E_{a,\text{cat}}/RT}}{Ae^{-E_a/RT}} = \frac{e^{-E_{a,\text{cat}}/RT}}{e^{-E_a/RT}}$$

$$\begin{aligned} E_{a,\text{cat}} &= E_a - RT \ln 1000 \\ &= 98 \text{ kJ} \cdot \text{mol}^{-1} - (8.31 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 1000) \\ &= 81 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Ans 4: (2% for each answer; 12% total)

(a) Overall reaction: $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

(b) Rate Law

Step 1 rate = $k[\text{O}_3][\text{NO}]$

Step 2 rate = $k[\text{NO}_2][\text{O}]$

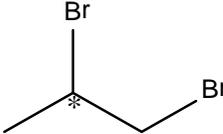
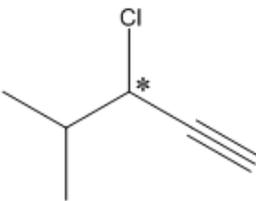
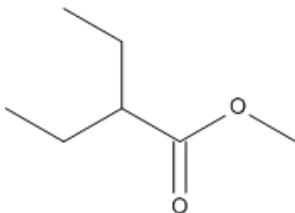
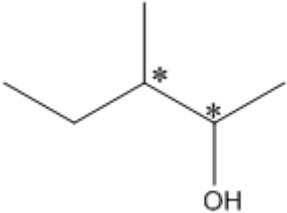
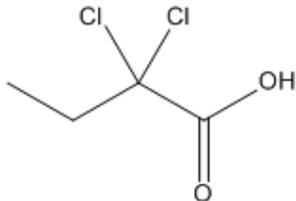
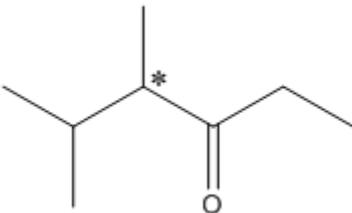
(c) reaction intermediate: NO_2

(d) catalyst: NO

(e) increases it.

(f) no effect.

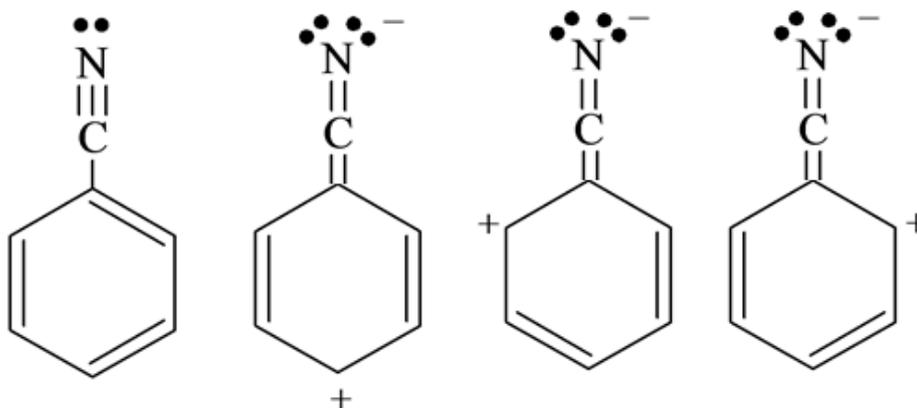
Ans 5: (每題 3 分，結構對才能開始給分，結構與星號佔 2 分，光學性 1 分
18% total)

a		optical active
b		optical active
c		not optical active
d		optical active
e		not optical active
f		optical active

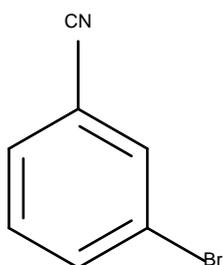
Ans 6: (2% for each answer, 12% total)

- (4) an electrophilic substitution reaction
- (3) an electrophilic addition reaction
- (2) a free-radical substitution reaction
- (7) a condensation reaction
- (7) a condensation reaction
- (1) a free-radical addition reaction

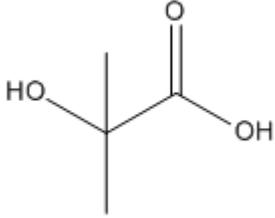
Ans 7: (2% for each molecular structure; 10% total)



The main product is



Ans 8: (2% for each answer, 6% total)

a	$\begin{array}{c} \text{CH} = \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$
b	
c	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{SH} \end{array} + \begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array}$

Ans 9: (2% for each question, 28 % total)

(1) D

(2) B

(3) E

(4) A

(5) A

(6) C

(7) C

(8) D

(9) B

(10) E

(11) D

(12) E

(13) A

(14) C