FINAL PAPER

PART B

1996

AUSTRALIAN CHEMISTRY OLYMPIAD

Please note that this answer book will be photocopied when returned and then split so that answers are sent to the appropriate markers. For this reason it is extremely important that you observe instructions 5 to 7.

Instruction to candidates

(1) You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.

(2) You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator and molecular models.

(3) You must attempt **all** questions.

(4) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

(5) Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.

(6) Your name must be written in the appropriate place on **each page** of your answers.

(7) Use **only black** or **blue ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

Question 1

Free-radical chain reactions are common in chemistry (eg. chlorination of alkanes, combustion). The general scheme is:

$$A \longrightarrow B^{\bullet} \qquad \text{Initiation}$$

$$B^{\bullet} + C \longrightarrow D + B^{\bullet} \qquad \text{Propagation}$$

$$2B^{\bullet} \longrightarrow E \qquad \text{Termination}$$

If the concentration of chain-propagating species ($B^{\bullet}$) is kept small compared with the concentration of reactant (C), then a small amount of A may be used to convert a large amount of C into D.

Free-radical polymerisation is a process whereby polymers (the long-chain molecules that make up plastics and rubbers) are produced from monomers (small, unsaturated organic compounds) with the aid of a radical-generating initiator. The reaction mechanism is:

$$\left.\begin{array}{l} I_2 \longrightarrow 2I^{\bullet} \\ I^{\bullet} + M \longrightarrow R_1^{\bullet} \end{array}\right\} \quad \text{Initiation}$$

$$\left.\begin{array}{l} R_1^\bullet + M \longrightarrow R_2^\bullet \\ . \\ . \\ . \\ R_i^\bullet + M \longrightarrow R_{i+1}^\bullet \end{array}\right\} \quad \text{Propagation}$$

$$R_i^\bullet + R_j^\bullet \longrightarrow P_i + P_j \qquad \text{Termination}$$

$$R_i^\bullet + M \longrightarrow P_i + R_1^\bullet \qquad \text{Transfer}$$

where I_2 is a molecule of initiator
$I^\bullet$ is an initiator fragment
M is a molecule of monomer
$R_i^\bullet$ is a growing polymeric radical of length i monomer units (IMMMMM…$M^\bullet$)
P_i is a dead polymer chain of length i monomer units (IMMMM…M)

If we define $[R]=\sum_i [R_i]$,

(a) Find an expression for the rate of conversion of monomer into polymer. (You may assume that the second initiation step is instantaneous and consumes negligible monomer)

(b) Derive an expression for the average length of the polymer chains formed (explain your reasoning). How would you alter the reaction conditions to shorten the chains formed? What other effect might this have on the formed polymer?

(c) Of course, some chains will be longer than the average, some shorter. Consider a population of radicals of length 1 at some time during the reaction - let’s call them B.

(i) Write down an expression for the number of these radicals that have not been “killed” (by termination or transfer) after an arbitrary time t. You may consider both the reaction volume and the concentration of monomer to be constant.

(ii) Now write down an expression predicting the number of chains with length N, called P(N). Explain your reasoning. (Hint: Consider the length to which a chain can grow in time t)

(d) It is noticed that during the course of many polymerisation reactions, the polymer formed precipitates out of solution. Explain qualitatively why you might expect polymers to exhibit lower solubility than their monomers in many solvents.

(e) Given that $\Delta H = \Delta U + P\Delta V$, predict qualitatively how the activation enthalpy, and hence rate, of the propagation reaction would change at high pressures. Explain your reasoning.

Question 2

(a) Molecular Orbital (MO) Theory was introduced by Mulliken in the 1940's and 1950's for which he won the 1964 Nobel Prize in Chemistry. It allows for the prediction of bond orders and paramagnetism of simple molecules.

(i) Construct a generalised MO energy level diagram for a diatomic molecule which possesses only 1s, 2s and 2p electrons. (Assume no 'mixing' of the 2s and 2p valence orbitals).

(iii) Which species in (ii) are expected to have the same stability?

(iv) Show by means of a MO energy level diagram that dioxygen is a biradical species.

(v) In analytical chemistry the Hg^{2+} ion is identified by reduction to Hg^+. However, the actual structure of the latter as determined from X-ray analysis is found to be the dimeric Hg_2^{2+} species. Using MO theory, show why the dimeric species is more stable than monomeric Hg^+.

(b) Nitric oxide (NO) is a simple molecule that has been known for a very long time and extensively studied. It recently aroused enormous new interest when it was discovered that this highly reactive, simple molecule plays a key role as a neurotransmitter in a wide range of biochemical systems. As with all biologically active chemical species a number of important questions immediately arise: How is the molecule made? Is it stored or made on demand? How is it stored? What are its targets? How is it removed whe,n no longer required? The inorganic chemist makes important contributions to answering these questions by designing simple model systems which mimic the chemistry occurring in the more complex living systems. Some observations on the chemistry of NO of relevance to understanding its participation in biochemical processes are the following:

1) Superoxide ion, O_2^- reacts rapidly with NO in water under physiological conditions to give the peroxonitrite ion, $[ONO_2]^-$.

2) The peroxonitrite ion reacts rapidly with aqueous CO_2, or HCO_3^-, to a give a species believed to be $[ONO_2CO_2]^-$.

3) Enzymes, called nitrite reductases and which contain Cu^+ ions in the active site, effect the reduction of NO_2^- to NO.

4) A sample of NO gas at 50 °C after rapid compression to 100 atmospheres shows a rapid drop in pressure at constant volume due to a chemical reaction. By the time the temperature has re-equilibrated to 50 °C, the pressure has dropped to less than 66 atmospheres.

(i) Identify those chemical species mentioned in (1) and (2) which possess an odd number of valence electrons. Suggest structures for $[ONO_2]^-$ and $[ONO_2CO_2]^-$, indicating the geometry about the N and C atoms.

(ii) To what classes of reaction do the reactions described in (1) and (2) belong?

(iii) Write a balanced equation for the reduction of NO_2^- with Cu^+ in aqueous acid solution.

(iv) If one of the products in (4) is N_2O what is the other product? How does the formation of these two products explain the experimental observations? To what class of reaction does this reaction belong?

Question 3

(a) Calculate the pH of a 0.100 M $NaHCO_3$ solution.
The acid dissociation constants for H_2CO_3 are $K_{a1} = 4.45 \times 10^{-7}$ and $K_{a2} = 4.69 \times 10^{-11}$.

(b) No net migration of an amino acid occurs in an electric field when the pH of the solution is such that the concentrations of the anionic and cationic forms are identical. This pH is called the *isoelectric point*. The zwitterionic form of the aminoacid, having both a positive and a negative charge, has no tendency to migrate in an electric field.
Show that for an aminoacid such as glycine (2-aminoethanoic acid), the isoelectric point is given by

$$[H^+] = (K_a K_w/K_b)^{1/2}$$

(c) A 0.0500 M U^{4+} solution was titrated with 0.1000 M Ce^{4+}. Both solutions are 1.0M in H_2SO_4. Under these conditions, Ce^{4+} is converted to Ce^{3+} ($E°_{Ce^{4+}/Ce^{3+}} = +1.44$ V) and U^{4+} to UO_2^{2+} ($E°_{UO_2^{2+}/U^{4+}} = +0.334$ V).

(i) Write the balanced equation for the redox reaction that occurs in this titration.

(ii) Write down an expression that relates $[U^{4+}]$ and $[Ce^{4+}]$ at the titration equivalence point.

(iii) Write down an expression that relates $[UO_2^{2+}]$ and $[Ce^{3+}]$ at the titration equivalence point.

(iv) Construct the titration curve <u>on the graph paper provided</u> (Y-axis = cell potential, X-axis = titrant volume) by calculating the cell-potential:
- at the equivalence point,

- half-way to the equivalence point,
- at 0.2 mL before the equivalence point,
- at 0.2 mL past the equivalence point, and
- at 2.0 mL past the equivalence point.

Question 4

Furopelargone-A, **1**, was isolated from *Pelargonium roseum*, and was shown to be an optically active compound with a molecular formula $C_{15}H_{22}O_2$. Furopelargone gave a positive test with 2,4-dinitrophenylhydrazine (2,4-DNP) and the ^1H nmr spectrum of **1** showed, amongst other features, two signals in the olefenic/aromatic region each corresponding to one proton. These two protons were shown to be on adjacent carbon atoms.

Reaction of **1** with $NaBH_4$ afforded **2**, $C_{15}H_{24}O_2$, which like **1** gave a positive iodoform test but unlike **1** no longer reacted with 2,4-DNP.

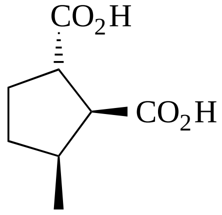
Controlled hydrogenation of **1** afforded **3,** $C_{15}H_{26}O_2$, which gave a derivative with 2,4-DNP.

The ^{13}C and ^1H nmr spectra of **3** showed a total of 4 CH_3 groups, two of which were incorporated in a single isopropyl unit; 4 CH_2 groups of which only one was adjacent to oxygen; and 6 CH groups of which only one was adjacent to oxygen.

Ozonolysis of **1** with careful oxidative work-up afforded a mixture of acids which was reacted with diazomethane to afford a corresponding mixture of methyl esters. Separation of this mixture afforded methyl 3-methyl-2-oxobutanoate and a compound **4**, $C_{10}H_{16}O_3$.

Reaction of **4** with dilute aqueous NaOH followed by acidification of the solution afforded **5**, $C_9H_{14}O_3$. This latter compound was soluble in aqueous $NaHCO_3$ and also gave a positive test with 2,4-DNP.

Sodium hypobromite (NaOBr) reacted with **5** to afford **6** which was shown to be enantiomeric with the known acid **7**.



7

(a) Deduce possible structures for **1** and explain your reasoning by proposing structures for compounds **2** - **6**.

(b) How do you account mechanistically for the formation of **5** during the ozonolysis of **1**? Note in answering this you must explain the loss of one carbon atom.

(c) How many stereoisomers could be produced in the conversion of **1** to **3**?