

FINAL PAPER

PART A

1994

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 nonprogrammable 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.

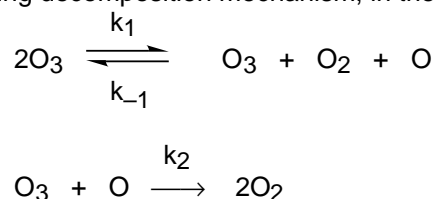
**Question 1**

The destruction of the Ozone layer is not unconnected to the Green House problem for the decomposition of ozone into diatomic oxygen may be catalysed in the presence of carbon dioxide. In a study designed to follow the kinetics of this decomposition the concentration of carbon dioxide was varied across two experiments.

Experiment 1 $[\text{CO}_2] = 0.01 \text{ mol L}^{-1}$ , $T=50^\circ\text{C}$	
<i>time / min</i>	<i>Total pressure / <math>10^{-5} \text{ Pa}</math></i>
0	0.533
30	0.599
60	0.633
$\infty$	0.666

Experiment 2 [CO <sub>2</sub> ] = 0.005 mol L <sup>-1</sup> , T=50°C	
time / min	Total pressure / 10 <sup>-5</sup> Pa
0	0.399
30	0.440
60	0.466
120	0.500
∞	0.533

- a) Determine the apparent order with respect to ozone and hence calculate the rate constant for both experiments. What are the half lives?
- b) Given that the value of the rate constant quadruples on going from 50 to 60 °C. Deduce the activation energy of this reaction.
- c) The following decomposition mechanism, in the absence of carbon dioxide, has been proposed:



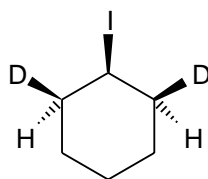
Deduce the resulting rate law. [ $k_2 \ll k_1 \approx k_{-1}$ ]

### Question 2

- (a) With the aid of clearly labelled diagrams illustrate the orbitals and hybrid orbitals used to account for the shapes and bonding in the following:
- (i) CH<sub>3</sub><sup>+</sup>      (ii) CH<sub>3</sub><sup>-</sup>      (iii) SF<sub>4</sub>      (iv) SOCl<sub>2</sub>      (v) NO<sub>3</sub><sup>-</sup>
- (b) Use the molecular orbital model to write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?
- (i) H<sub>2</sub><sup>-</sup>      (ii) O<sub>2</sub>      (iii) CN<sup>+</sup>      (iv) CN      (v) CN<sup>-</sup>
- (c) How many unpaired electrons do each of the following complex ions have in their ground state electron configurations? Your answer should include a clearly labelled d-orbital splitting diagram for each species.
- (i) CoCl<sub>4</sub><sup>2-</sup>      (ii) Co(CN)<sub>6</sub><sup>4-</sup>      (iii) Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>      (iv) Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>      (v) CoF<sub>6</sub><sup>3-</sup>
- (d) Draw and name all the possible linkage, geometric, and optical isomers of [Co(en)<sub>2</sub>(SCN)Cl]Cl.

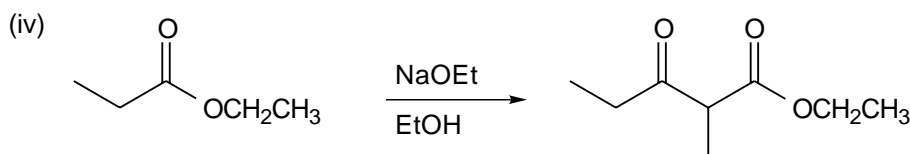
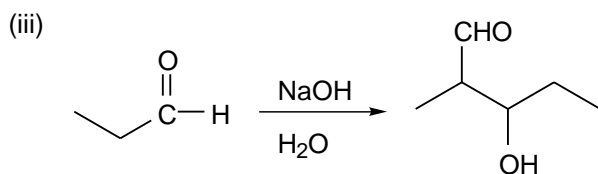
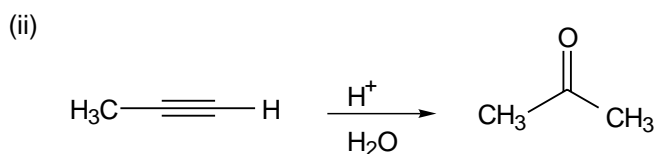
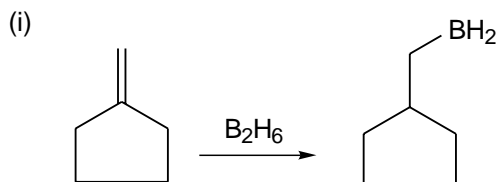
### Question 3

- (a) The deuterated iodocyclohexane shown below is known to undergo E2 elimination upon treatment with sodium ethoxide in ethanol to yield a deuterated cyclohexene. By following the reaction mechanism deduce how many deuteriums (D) will be present in the final product.

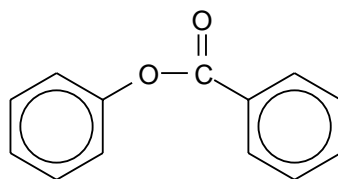


- (b) Bromine adds to *trans*-2-butene in dichloromethane as solvent to give only the optically inactive *meso*-2,3-dibromobutane, but if water is the solvent a bromohydrin (a compound bearing OH and Br on adjacent carbons) is obtained.
- (i) Using appropriate saw-horse diagrams, present a mechanism to account for the stereospecific addition of bromine to the alkene.

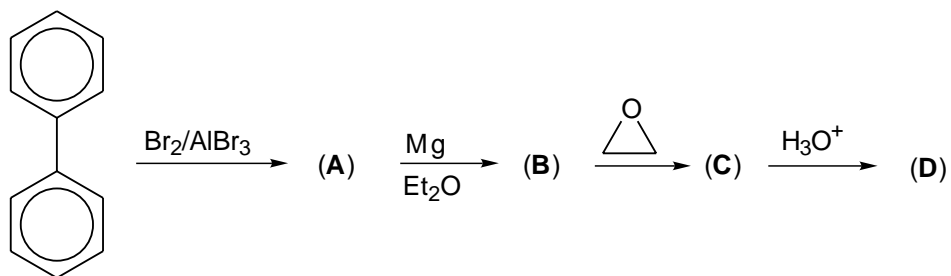
- (ii) Expand this mechanism to accommodate formation of the bromohydrin.  
 (iii) Predict the stereochemistry of the bromohydrin.  
 (iv) Designate the chiral centres in the bromohydrin product(s) as **R** or **S** as is appropriate .
- (c) Write mechanisms to account for each of the following reactions



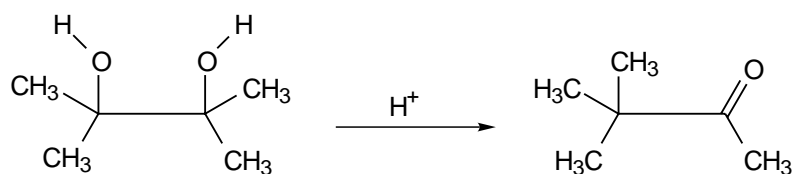
- (d) (i) Predict the **major** product expected from the reaction of  $\text{Br}_2$  and  $\text{AlBr}_3$  with phenyl benzoate (shown below) being sure to explain your reasoning



- (ii) Indicate the intermediates (**A-C**) and final product (**D**) in the following reaction sequence



- (e) Rearrangements of the carbon skeletons of electron deficient species are well documented in organic chemistry. Devise a plausible explanation for the well known *pinacol rearrangement*,



based upon what you already know concerning the behaviour of alcohols in acidic solution.

- (f) A compound (**A**) has been found to have the molecular formula  $C_7H_{12}$ . It reacts with dilute potassium permanganate and compound (**B**) ( $C_7H_{14}O_2$ ) is formed. If **A** is treated with perbenzoic acid in chloroform solution, compound (**C**) ( $C_7H_{12}O$ ) is formed. When **C** reacts with dilute sulfuric acid compound (**D**), ( $C_7H_{14}O_2$ ) is formed. **D** is stereoisomer with **B**.

Ozonolysis of **A** gives 2,6-heptanedione.

Assign the structures of compounds **A**  $\rightarrow$  **D**.

#### Question 4

A traditional method for the analysis of calcium in a sample is to dissolve the sample and then precipitate  $Ca^{2+}$  as "insoluble" calcium oxalate by addition of oxalate ion,  $C_2O_4^{2-}$ .

In this gravimetric (= "measurement by weighing") procedure, the precipitate, which is obtained as a monohydrate ( $CaC_2O_4 \cdot H_2O$ ) is carefully collected, washed, dried and weighed. The amount of calcium in the original sample can be calculated from the mass of calcium oxalate precipitate. Simple!

- a) Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

$$K_{sp}(CaC_2O_4) = 2.3 \times 10^{-9} \text{ and for oxalic acid, } pK_{a1} = 1.27 \text{ and } pK_{a2} = 4.27$$

Relative atomic masses: H 1.008; C 12.01; O 16.00; Ca 40.08;

- b) Before the analysis can be performed, the buffer solution needs to be prepared.

Calculate the volume of 0.0968 M NaOH that needs to be added to 100 mL 1.024 M acetic acid so that, after dilution of this mixture to 1000 mL in a volumetric flask, the pH will be 4.00. The  $pK_a$  of acetic acid is 4.76.

To determine the amount of calcium carbonate in a commercial calcium supplemented vitamin tablet, the following procedure was used:

- Step 1 The tablet was weighed in a 100 mL beaker, then crushed.
- Step 2 Ten mL of the pH 4 acetate buffer (prepared above) was added and the solution was warmed to  $60^\circ C$  to dissolve the tablet.
- Step 3 Excess 0.5 M ammonium oxalate solution was added to precipitate the calcium.
- Step 4 The precipitate was carefully collected on a pre-weighed porous glass filter crucible, by sucking the reaction mixture through the filter using a water-jet vacuum pump.
- Step 5 The precipitate was carefully washed with distilled water (adjusted to pH 4 by a few drops of buffer) and then sucked nearly dry on the water-jet pump.
- Step 6 The filter crucible was carefully heated to  $100-110^\circ C$  for a few hours to dry the precipitate, cooled to room temperature then re-weighed.

The following results were obtained for three separate tablets:

	mass tablet (g)	mass filter crucible (g)	
		empty	with precipitate
1	1.5214	10.3248	12.5023
2	1.5032	10.6172	12.7277
3	1.5148	10.1084	12.2734

- c) Write down the balanced chemical equations for steps 2 and 3.
- d) Calculate the mass percentage of calcium carbonate in each tablet. Take care with significant figures.
- e) Calculate the error in your calcium carbonate results, caused by neglecting the solubility of calcium oxalate at pH 4.
- f) Is pH 4 acetate buffer a good choice for this analysis? Suggest a better buffer and explain your reasoning.
- g) Estimate the uncertainty in the calcium carbonate results. You can assume that the chemist performs the procedure very carefully, but that the balance that she uses has an uncertainty of  $\pm 0.0002$  g.

Use the following rules for calculation of uncertainty  $e_x$  in a result,  $x$ , if  $y$  and  $z$  have uncertainties  $e_y$  and  $e_z$  respectively:

If  $x = y + z$  or  $y - z$  then  $e_x = e_y + e_z$  (ie the *absolute* uncertainties are added)

If  $x = y z$  or  $y/z$  then  $\frac{e_x}{x} = \frac{e_y}{y} + \frac{e_z}{z}$  (ie the *relative* uncertainties are added)

- h) In the light of your estimated uncertainty for the calcium carbonate results, do all three tablets appear to be identical? Which step(s) in the analysis might have caused this "problem". Explain.