Country:	Language:

37th International Chemistry Olympiad

Taipei, Taiwan

Practical Examination

Tuesday, 19 July 2005

Country:	Language:

Important Remarks

- The plastic bag you got upon entering the laboratory is the unknown samples for experiment 2. Put it inside the basket on your bench for later use.
- At all times while you are in the laboratory you should wear safety spectacles or your own spectacles if they have been approved.
- Eating of any kind of food is strictly prohibited in the laboratory.
- When you enter the laboratory, check the place of the safety shower.
- Participants are expected to work safely, to behave socially and to keep equipment and work environment clean. Do not hesitate to ask a laboratory assistant if you have any questions concerning safety issues.
- **Work may only begin when the start signal is given.**
- You have 5 hours to complete all of the experimental tasks, and record your results on the answer sheets. There will be a pre-warning 30 minutes before the end of your time. You must stop your work immediately after the stop command is given. A delay in doing this by 5 minutes will lead to cancellation of the current task and will result in zero points for that task.
- **This practical examination comprises two experiments. In order to use the available time efficiently, you will start working on the organic chemistry experiment up to the point where you are instructed to work on the analytical chemistry experiment. Then you will finish the work on the organic chemistry experiment. The second part of the organic experiment (experiment 1) will need at least 1 hour.**
- **Use only the pen and calculator provided.**
- Write your name and personal identification code (in the back of your name card) on every answer sheets.
- All results must be written in the answer boxes on the answer sheets. Data written elsewhere will not be marked. Do not write anything in the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the laboratory assistant.
- When you have finished the examination, you must put all answer sheets into the envelope provided. Only papers in the envelope will be marked.
- Do not leave the examination room until you have permission to do so.
- Use only the tools provided.
- There are total **5** pages of answer sheets, **4** for organic and **1** for analytical experiment, respectively.
- 4 blank draft papers (will not be marked) are provided, more are available on request
- An official English-language version is available only on request.

Disposal of waste chemicals, spills, and glassware

There are three waste containers in the lab, one for organic filtrates and organic washings, one for solid wastes, and one for broken glass.

Cleaning up

Please keep your work area clean. Wipe your lab bench with a wet tissue when you are finished.

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Periodic table of elements

with atomic masses / u

1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.3	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po 208.98	85 At 209.99	86 Rn 222.02
87 Fr 223	88 Ra 226	89-103	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 264	108 Hs 265	109 Mt 268									
		57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 144.92	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
		89 Ac 227	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 262	

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Organic synthesis

Equipment list

equipment	No.	equipment	No.
Hot plate/stirrer with stand	1	Weighing paper	10
Stirrer	2	Sample vial (20 mL) (**blue label** labelled with your student code and ^{1}H NMR)	1
Stirrer retriever	Shared by 2 persons	Sample vial (20 mL) (**pink label** labelled with your student code and $[\alpha]_D$)	1
Filtration pump	Shared by 2 persons	Glass rod	1
Clamp with holder	3	Spatula	2
thermometer	1	Septa	2
Pasteur pipette	5	Water bath (stainless steel)	1
Pipette bulb	2	Ice bath (Styrofoam)	1
Graduated cylinder (10 mL)	1	Needle	1
Graduated cylinder(25 mL)	1	Water bottle with Deionized H_2O	1
Round bottom flask (25 mL)	1	Glove (cotton)	1 pair
Round bottom flask (50 mL)	1	Glove (latex) on central bench	
Filter, Fritted (50 mL) (labelled with your student code)	1	Flask holder	1 pc
Filter, Fritted (70 mL) (labelled with your student code)	1	Paper towel	1 roll
Filtration flask with rubber (250 mL)	1	Kimwipes	1 box
Condenser	1	Glass funnel	1
Teflon sleeve for condenser *(you can trim off 1 cm from the smaller end for a better fit)*	1	Beaker (800 mL)	1
Safety goggles	1	Beaker (400 mL)	1

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Chemical list

chemicals	formula	formula weight	amount	Risk statements	Safety statements
ethanol	C_2H_5OH	46.07	50 mL	11	7-16
pre-mixed solvents ethylene glycol:ethanol (2:9)	$(CH_2OH)_2$	-	50 mL	22	-
benzoylformic acid	$C_8H_6O_3$	150.13	written on sample vial	36/37/38	26-28-36
ammonium formate	HCO_2NH_4	63.06	7.57 g	36/37/38	26-36
D,L-phenylglycine	$C_8H_9NO_2$	151.16	written on sample vial (to be provided for step 2)	-	22-24/25
Pentamethylcyclopentadienyl-rhodium(III) chloride, dimer	$[(CH_3)_5C_5RhCl_2]_2$	-	37.2 mg	20/21/22, 36/37/38	26, 36
(1*S*)-(+)-10-camphorsulfonic acid (+)-(CSA)	$C_{10}H_{16}O_4S$	232.30	1.80 g	34	26-36/37/39-45

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Risk statements

R 11	Highly flammable.
R 20	Harmful by inhalation.
R 22	Harmful if swallowed.
R 25	Toxic if swallowed.
R 31	Contact with acids liberates toxic gas.
R 32	Contact with acid liberates very toxic gas.
R 34	Causes burns.
R 35	Causes severe burns.
R 36	Irritating to eyes.
R 37	Irritating to respiratory system.
R 38	Irritating to skin.
R 40	Limited evidence of a carcinogenic effect
R 41	Risk of serious damage to the eyes.
R 43	May cause sensitization by skin contact.
R 50	Very toxic to aquatic organisms.
R 52	Harmful to aquatic organisms.
R 53	May cause long-term adverse effects in the aquatic environment.

Combination of risk statements

R 20/21/22	Harmful by inhalation, in contact with skin, and if swallowed.
R 36/37/38	Irritating to eyes, respiratory system and skin.

Safety statements

S 7	Keep container tightly closed.
S 13	Keep away from food, drink and animal foodstuffs.
S 16	Keep away from sources of ignition - No smoking.
S 22	Do not breathe dust.
S 23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S 23.2	Do not breathe vapor.
S 24	Avoid contact with skin.
S 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 28	After contact with skin, wash immediately with plenty of soap-suds.
S 30	Never add water to this product.
S 36	Wear suitable protective clothing.
S 37	Wear suitable gloves.
S39	Wear eye / face protection.
S 41	In case of fire and/or explosion do not breathe fumes.
S 45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 60	This material and its container must be disposed of as hazardous waste.
S 61	Avoid release to the environment. Refer to special instructions / Safety data sheets.

Combination of safety statements

S 24/25	Avoid contact with skin and eyes.
S 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S 36/37	Wear suitable protective clothing and gloves.
S 37/39	Wear suitable gloves and eye/face protection.

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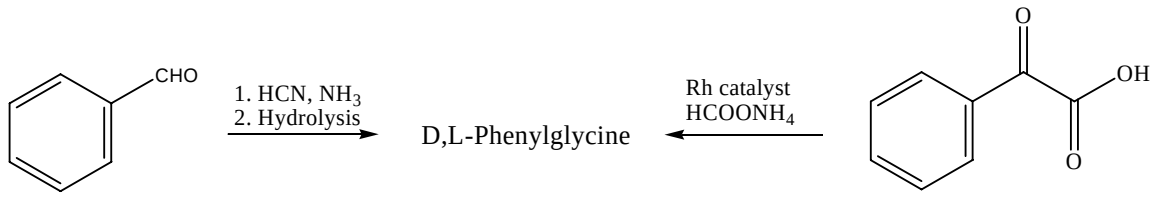
Experiment 1

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β-lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH_3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



Benzaldehyde D,L-phenylglycine Benzoylformic acid

In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as R- and S- isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H_2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H_2O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Caution: You have to wear latex gloves during all operation for practical task 1.

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (**NOTE: *irritant, do not contact with skin***), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (**NOTE:**

the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 mL of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (**NOTE: the solvent is air cooled, so there is no tap water running through the condenser.**) The temperature of the water bath needs to be maintained in the range of 68 to 72 °C by adjusting the thermostat of the hot plate/stirrer.

3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.

4. Add 15 mL of deionized water to the resulting mixture and stir for 10 minutes.

5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 mL each). For each washing, ***break the aspirator pressure***, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.

6. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 °C for 1.5 hour.

During the drying period you can start working on Experiment 2 (Analytical Experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

7. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The

purity of the product will be determined by ^{1}H NMR spectrum analysis. Turn in the product in a vial (**blue label** with ^{1}H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

Step 2. Enantiomeric resolution of D,L-phenylglycine by (+)-camphorsulfonic acid [(+)-CSA]

1. To a 25 mL round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 mL) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.

2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.

3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 mL each).

4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).

5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (**pink label** labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

The organization committee will weigh the resolved product (from the fritted glass funnel) for students who fail to finish the procedure in time. However, 15 penalty points will be taken.

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Experiment 2

Identification of Unknown Inorganic Samples

Note

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in the equipment and reagent list.

(3) **Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.**

(4) The volume of each unknown solution is about 1.5 mL (about 30 drops). **No more reagents or samples will be provided**.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) **You will get 8 points for each correct identification.**

Introduction

There are 12 unknown samples in your plastic bag：9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the **List of Unknown Inorganic Samples** carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 mL solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol/L).

The unknown samples are as follows:

HCl	H_2O_2	H_2SO_4	$ZnCl_2$	NH_4SCN
NaOH	Na_2CO_3	Na_2SO_3	$BaCl_2$	$K_4Fe(CN)_6$

Note

(1) Two unknown samples are duplicates.

(2) The hydrated H_2O of crystal is omitted in the formulas listed above.

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On your lab bench, there is a plastic basket which contains the equipments, unknown samples, and reagents to be used in this task.

Equipment list

equipment	No.	equipment	No.
Pt wire electrode	1	Au wire electrode	1
Battery case	1	Battery	2
Pallet	1	Black film (round)	1
Scissors	1	Dropper (1 mL)	5
Coffee stirrer	2		

Reagent list

Reagent	Conc.	Reagent	Conc.
KI	0.1M	pp (phenolphthalein)	0.01%
$FeCl_3$	0.1M	Starch solution	0.01%

Risk and safety statements

Chemicals	Formula	Risk statements	Safety statements
Hydrochloric acid	HCl	36/37/38	26
Sulfuric acid	H_2SO_4	35	26-30-45
Sodium hydroxide solution	NaOH	35	26-36/37/39-45
Hydrogen peroxide solution	H_2O_2	22-41	26-39
Sodium carbonate solution	Na_2CO_3	36	22-26
Barium chloride solution	$BaCl_2$	20-25	45
Sodium sulfite solution	Na_2SO_3	31-36/37/38	26-36
Zinc chloride solution	$ZnCl_2$	22-34-50/53	26-36/37/39-45-60-61
Potassium hexacyanoferrate (II) solution	$K_4Fe(CN)_6$	32	22-24/25
Ammonium thiocyanate solution	NH_4SCN	20/21/22-32-52/53	13-61
Iron (III) chloride (solid)	$FeCl_3$	22-34	26-36/37/39-45
Potassium iodide (solid)	KI	-	22-24/25 *
Starch solution	-	-	-
Phenolphthalein indicator		40	36/37

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2-1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

Note

After you have finished your work, please put the two electrodes (Pt and Au wires) and two batteries back in their original plastic bags, respectively, then return all equipment and reagents (include unknown samples) to the original places (in the plastic basket).

2-2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is $ZnCl_2$.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).