



Washington, D.C. • USA



# Practical Examination

44th International  
Chemistry Olympiad

July 24, 2012

United States  
of America

# Instructions (Task 1)

- This examination has **10 pages** for practical Task 1 and answer sheets.
- You have **15 minutes** to read this booklet **completely** before starting the experiments.
- You have **2 hours 15 minutes** to complete the practical **Task 1**.
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. A delay in doing this by 5 minutes will lead to cancellation of your practical exam. After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following item should be **left on your bench**:
  - The problem / answer booklet (this booklet)
- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own prescription safety glasses if they have been approved. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the **pen** provided, **not a pencil**, for writing the answers.
- Use the calculator provided.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the backside of the sheets if you need scratch paper.
- Use the container labeled as “**Used Vials**” to dispose sealed vials with reaction solutions.
- Use the container labeled as “**Liquid Waste**” to dispose the waste solutions.
- Use the container labeled as “**Broken Glass Disposal**” to dispose the ampule fragments.
- Chemicals and lab ware will be **refilled or replaced** without penalty only for the first incident. Each further incident will result in the **loss of 1 point** from your 40 practical exam points.
- The official English version of this examination is available on request only for clarification.

## Chemicals and Equipment (Task 1)

**Chemicals (the actual labeling for each package is given in bold font)**

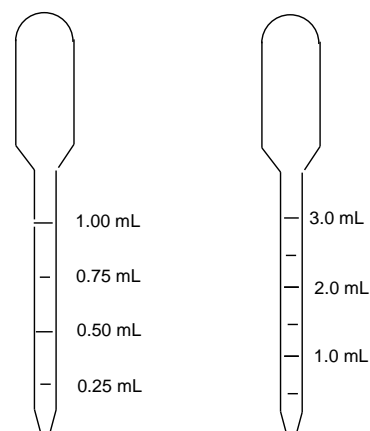
	Risk Phrase <sup>+</sup>	Safety Phrase <sup>+</sup>
~ <b>2 M HCl</b> , <sup>*</sup> solution in water, 50 mL in a bottle	R34, R37	S26, S45
~ <b>0.01 M KI<sub>3</sub></b> , <sup>*</sup> solution in water, 10 mL in a bottle, labeled " <b>I<sub>2</sub></b> ".		
Acetone, <b>(CH<sub>3</sub>)<sub>2</sub>CO</b> , M = 58.08 g mol <sup>-1</sup> , density = 0.791 g mL <sup>-1</sup> , 10.0 mL in a vial	R11, R36, R66, R67	S9, S16, S26
<b>Acetone-d<sub>6</sub></b> , (CD <sub>3</sub> ) <sub>2</sub> CO, M = 64.12 g mol <sup>-1</sup> , density = 0.872 g mL <sup>-1</sup> , 3.0 mL in a pre-scored ampule	R11, R36, R66, R67	S9, S16, S26

<sup>+</sup> See page 3 for definition of Risk and Safety Phrases.

<sup>\*</sup> The exact molarity is indicated on the label, with the concentration given before the name of the substance.

### **Equipment - Kit #1**

- One glass bottle filled with distilled water
- **Fifteen** 20-mL screw-cap glass vials with Teflon-lined screw-caps
- **Ten** 1-mL polyethylene transfer pipettes graduated in 0.25 mL increments (see drawing in the right).
- **Ten** 3-mL polyethylene transfer pipettes graduated in 0.50 mL increments (see drawing in the right).
- One digital timer (stopwatch)



**Name:**

**Code: TJK**

## **Risk and Safety Phrases (Task 1)**

R11 Highly flammable

R34 Causes burns

R36 Irritating to eyes

R37 Irritating to respiratory system

R66 Repeated exposure may cause skin dryness or cracking

R67 Vapors may cause drowsiness and dizziness

S9 Keep container in a well-ventilated place

S16 Keep away from sources of ignition

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

S45 In case of accident or if you feel unwell, seek medical advice immediately

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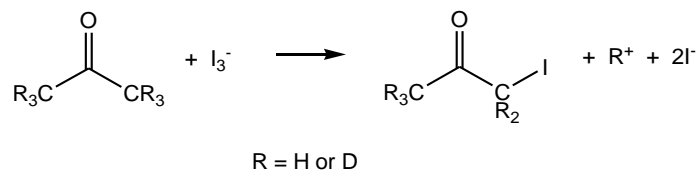
**Task 1****18% of the total**

a	b	c	d	e	f	g	Task 1	18%
10	2	10	12	16	12	8	70	

## Kinetics, Isotope Effect, and Mechanism of Iodination of Acetone

Discoveries about the mechanisms of chemical reactions underlie advances in catalysis and synthesis. One of the most powerful tools for probing reaction mechanisms is the study of kinetics because the ways in which reaction rates vary with reaction conditions follow directly from the mechanism of reaction. A second powerful tool is the study of isotopically substituted molecules. While isotopes show **similar reactivity**, there are slight differences in **reaction rates** as a function of nuclear mass.

In this task you will use both kinetics and isotope effects to provide information about the iodination of acetone in acidic aqueous solution:



The reaction takes place with a rate law

$$\text{Rate} = k[\text{acetone}]^m[\text{I}_3^-]^n[\text{H}^+]^p$$

where the rate constant  $k$  and the **integer** reaction orders  $m$ ,  $n$ , and  $p$  are for you to determine.

You will also compare the reactivity of acetone with that of acetone- $d_6$ , where the six atoms of protium ( $^1\text{H}$ ) have been replaced by deuterium ( $^2\text{H}$ , D), to determine the isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of the reaction. From these data you will make inferences about the mechanism of this reaction.

***Please read the whole description of this task and plan your work before you begin.***

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Code: TJK

## Procedure

Reaction rates are dependent on temperature. Record the temperature in the room you are working in (ask the room assistant):

°C

### Instructions for using the digital timer (stopwatch)

- (1) Press the [MODE] button until the **COUNT UP** icon is displayed.
- (2) To begin timing, press the [START/STOP] button.
- (3) To stop timing, press the [START/STOP] button again.
- (4) To clear the display, press the [CLEAR] button.

### General Procedure

\*Measure the volumes of **hydrochloric acid**, **distilled water**, and **potassium triiodide solution** (labeled as “I<sub>2</sub>”) that you choose into the reaction vessel. The initial concentrations of the reagents in the reaction mixtures should be in the ranges given below (you need not explore the full ranges given, but your values should not be significantly outside these ranges):

- [H<sup>+</sup>]: Between 0.2 and 1.0 M
- [I<sub>3</sub><sup>-</sup>]: Between 0.0005 and 0.002 M
- [acetone]: Between 0.5 and 1.5 M

**\*To initiate the reaction**, add the chosen volume of **acetone** to the solution containing the other reagents, quickly cap (close) the reaction vessel, **start the timer**, shake the vial vigorously one time, then put it aside on a white background.

Report the volumes of reagents that you use in the table provided in (a). When setting up and running a reaction **do not hold or touch the vial below the level of liquid in it**. The progress of the reaction can be monitored visually by watching the **disappearance of the yellow-brown color of the triiodide ion**.

Record the time required for the color to disappear. When the reaction is complete, set aside the vessel, and leave it sealed so that you do not expose yourself to iodoacetone vapors.

Repeat as often as desired with different concentrations of reagents. Report the concentrations of the reagents that you use in the **tables in (c)** below.

Hint: change ONLY one concentration at a time.

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\*After you have studied the rate of reaction of acetone, you should examine the rate of reaction of acetone- $d_6$ . Note that while you have an ample supply of acetone, you will be given **only 3.0 mL of acetone- $d_6$**  because of the greater expense of the isotopically labeled material. Therefore, any refilling of acetone- $d_6$  will be accompanied by a one point penalty. **When you need to use this reagent, raise your hand and the lab supervisor will open the sealed ampule for you.** The reactions of deuterium-substituted compounds are generally **slower** than those of protium-substituted compounds. You would thus be well advised to use reaction conditions that promote faster reactions when working with  $(CD_3)_2CO$ .

When you are finished working:

- a) empty the water bottle and place it along with any unused equipment back to the box labeled "Kit #1";
- b) place used pipettes and sealed used vials in designated containers under the hoods;
- c) Use a container labeled **Broken Glass Disposal** to dispose of all parts of the empty ampule.

You may clean up your area after the STOP command has been given.

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a. Record your results for acetone,  $(\text{CH}_3)_2\text{CO}$ , in the table below. *You need not fill the entire table.*

Run #	Volume HCl solution, mL	Volume $\text{H}_2\text{O}$ , mL	Volume $\text{I}_3^-$ solution, mL	Volume $(\text{CH}_3)_2\text{CO}$ , mL	Time to disappearance of $\text{I}_3^-$ , s
1					
2					
3					
4					
5					
6					
7					
8					

b. Record your results for acetone- $d_6$ ,  $(\text{CD}_3)_2\text{CO}$ , in the table below. *You need not fill the entire table.*

Run #	Volume HCl solution, mL	Volume $\text{H}_2\text{O}$ , mL	Volume $\text{I}_3^-$ solution, mL	Volume $(\text{CD}_3)_2\text{CO}$ , mL	Time to disappearance of $\text{I}_3^-$ , s
1d					
2d					
3d					
4d					



Name:

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c. Use the following tables to calculate concentrations and average rates for the reactions you studied. Assume that the volume of each reaction mixture is equal to the sum of volumes of its constituent solutions.

**You need not use all of your runs in your calculation of  $k$  (parts e and f), but you must indicate which run or runs you used in your calculation by checking the appropriate box in the right-hand column.**

**$(\text{CH}_3)_2\text{CO}$ :**

Run #	Initial $[\text{H}^+]$ , M	Initial $[\text{I}_3^-]$ , M	Initial $[(\text{CH}_3)_2\text{CO}]$ , M	Average rate of disappearance of $\text{I}_3^-$ , $\text{M s}^{-1}$	Run used in calculating $k_{\text{H}}$ ?	
					Yes	No
1					<input type="checkbox"/>	<input type="checkbox"/>
2					<input type="checkbox"/>	<input type="checkbox"/>
3					<input type="checkbox"/>	<input type="checkbox"/>
4					<input type="checkbox"/>	<input type="checkbox"/>
5					<input type="checkbox"/>	<input type="checkbox"/>
6					<input type="checkbox"/>	<input type="checkbox"/>
7					<input type="checkbox"/>	<input type="checkbox"/>
8					<input type="checkbox"/>	<input type="checkbox"/>

**$(\text{CD}_3)_2\text{CO}$ :**

Run #	Initial $[\text{H}^+]$ , M	Initial $[\text{I}_3^-]$ , M	Initial $[(\text{CD}_3)_2\text{CO}]$ , M	Average rate of disappearance of $\text{I}_3^-$ , $\text{M s}^{-1}$	Run used in calculating $k_{\text{D}}$ ?	
					Yes	No
1d					<input type="checkbox"/>	<input type="checkbox"/>
2d					<input type="checkbox"/>	<input type="checkbox"/>
3d					<input type="checkbox"/>	<input type="checkbox"/>
4d					<input type="checkbox"/>	<input type="checkbox"/>

Name:

Code: TJK

d. Give the **integer** reaction order in acetone, triiodide, and hydrogen ion.

$$\text{rate} = -\frac{d[I_3^-]}{dt} = k[(CH_3)_2CO]^m[I_3^-]^n[H^+]^p$$

$m =$

$n =$

$p =$

e. Calculate the rate constant  $k_H$  for the reaction of acetone,  $(CH_3)_2CO$ , and indicate the units.

$k_H =$

f. Calculate the rate constant  $k_D$  for the reaction of acetone- $d_6$ ,  $(CD_3)_2CO$ , and calculate the value of  $k_H/k_D$  (the isotope effect of the reaction).

$k_D =$

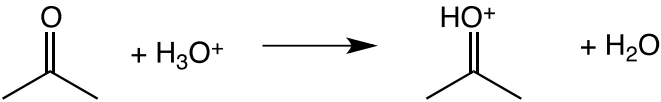
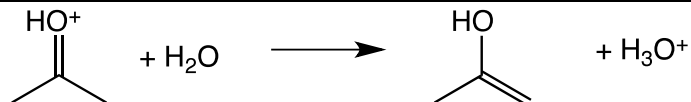
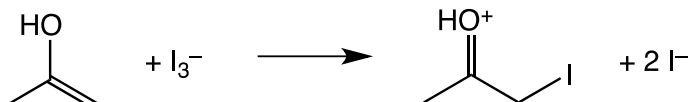
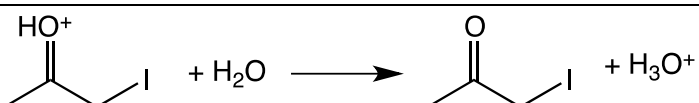
$k_H/k_D =$

Name:

Code: TJK

g. From the kinetic and isotope effect data you may draw certain conclusions about the reaction mechanism. Shown below is a reasonable mechanism for the iodination of acetone. One reaction is the rate-determining step (R.D.S.), with all previous steps rapidly achieving an equilibrium that strongly favors the reactants.

In the box in the first column on the right next to each step, place a check mark (✓) if your *experimentally measured rate law* (part d) is **consistent** with that step being rate-determining and an **X** if your measured rate law is **inconsistent** with that step being rate-determining. In the box in the second column on the right next to each step, place a check mark (✓) if your *experimentally measured isotope effect* (part f) is **consistent** with that step being rate-determining and an **X** if your measured isotope effect is **inconsistent** with that step being rate-determining.

	R.D.S. consistent with rate law?	R.D.S. consistent with isotope effect?
		
		
		
		

Name:

**Code: TJK**

1																	2			
1	1 1.00794 H 0.28																			
2	3 6.941 Li	4 9.01218 Be													5 10.811 B 0.89	6 12.011 C 0.77	7 14.0067 N 0.70	8 15.9994 O 0.66	9 18.9984 F 0.64	10 20.1797 Ne 1.50
	11 22.9898 Na	12 24.3050 Mg													13 26.9815 Al	14 28.0855 Si 1.17	15 30.9738 P 1.10	16 32.066 S 1.04	17 35.4527 Cl 0.99	18 39.948 Ar 1.80
3																				
	19 39.0983 K	20 40.078 Ca	21 44.9559 Sc	22 47.867 Ti 1.46	23 50.9415 V 1.33	24 51.9961 Cr 1.25	25 54.9381 Mn 1.37	26 55.845 Fe 1.24	27 58.9332 Co 1.25	28 58.6934 Ni 1.24	29 63.546 Cu 1.28	30 65.39 Zn 1.33	31 69.723 Ga 1.35	32 72.61 Ge 1.22	33 74.9216 As 1.20	34 78.96 Se 1.18	35 79.904 Br 1.14	36 83.80 Kr 1.90		
4	37 85.4678 Rb	38 87.62 Sr	39 88.9059 Y	40 91.224 Zr 1.60	41 92.9064 Nb 1.43	42 95.94 Mo 1.37	43 (97.905) Tc 1.36	44 101.07 Ru 1.34	45 102.906 Rh 1.34	46 106.42 Pd 1.37	47 107.868 Ag 1.44	48 112.41 Cd 1.49	49 114.818 In 1.67	50 118.710 Sn 1.40	51 121.760 Sb 1.45	52 127.60 Te 1.37	53 126.904 I 1.33	54 131.29 Xe 2.10		
	55 132.905 Cs	56 137.327 Ba	57-71 La-Lu	72 178.49 Hf 1.59	73 180.948 Ta 1.43	74 183.84 W 1.37	75 186.207 Re 1.37	76 190.23 Os 1.35	77 192.217 Ir 1.36	78 195.08 Pt 1.38	79 196.967 Au 1.44	80 200.59 Hg 1.50	81 204.383 Tl 1.70	82 207.2 Pb 1.76	83 208.980 Bi 1.55	84 (208.98) Po 1.67	85 (209.99) At	86 (222.02) Rn 2.20		
5	87 (223.02) Fr	88 (226.03) Ra 2.25	89-103 Ac-Lr	104 (261.11) Rf	105 (262.11) Db	106 (263.12) Sg	107 (262.12) Bh	108 (265) Hs	109 (266) Mt	110 (271) Ds	111 (272) Rg	112 (285) Cn	113 (284) Uut	114 (289) Fl	115 (288) Uup	116 (292) Lv	117 (294) Uus	118 (294) Uuo		
6	57 138.906 La 1.87	58 140.115 Ce 1.83	59 140.908 Pr 1.82	60 144.24 Nd 1.81	61 (144.91) Pm 1.83	62 150.36 Sm 1.80	63 151.965 Eu 2.04	64 157.25 Gd 1.79	65 158.925 Tb 1.76	66 162.50 Dy 1.75	67 164.930 Ho 1.74	68 167.26 Er 1.73	69 168.934 Tm 1.72	70 173.04 Yb 1.94	71 174.04 Lu 1.72					
	89 (227.03) Ac 1.88	90 232.038 Th 1.80	91 231.036 Pa 1.56	92 238.029 U 1.38	93 (237.05) Np 1.55	94 (244.06) Pu 1.59	95 (243.06) Am 1.73	96 (247.07) Cm 1.74	97 (247.07) Bk 1.72	98 (251.08) Cf 1.99	99 (252.08) Es 2.03	100 (257.10) Fm	101 (258.10) Md	102 (259.1) No	103 (260.1) Lr					
7																				

# Instructions (Task 2)

- This examination has **13** pages for Task 2 and answer sheets.
- You have 15 minutes to read this booklet before starting the experiments.
- You have **2 hours 45 minutes** to complete the practical **Task 2**. When planning your work, please note that one of the steps requires **30 minutes**.
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is announced. A delay in doing this by 5 minutes will lead to cancellation of your practical exam. After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left on your bench**:

The problem / answer booklet (this booklet)

One TLC plate in zipper storage bag with student code

The vial labeled “Product”

- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own prescription safety glasses if they have been approved. Use the **pipette filler bulb** provided. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- You are allowed to work only in the space allocated for you.
- Use only the **pen** provided, not a pencil, for writing the answers.
- Use the calculator provided.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the backside of the sheets if you need scratch paper.
- Use the container labeled as “**Broken Glass Disposal**” to dispose used vials.
- Use the **container** labeled as “**Liquid Waste**” to dispose all waste solutions.
- Chemicals and lab ware will be **refilled or replaced** without penalty only for the first incident. Each further incident will result in the **loss of 1 point** from your 40 practical exam points.
- The official English version of this examination is available on request only for clarification.

Name:

Code: TJK

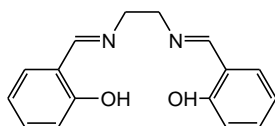
## Chemicals and Equipment (Task 2)

**Chemicals and materials (the actual labeling for each package is given in bold font)**

	Risk Phrase <sup>+</sup>	Safety Phrase <sup>+</sup>
<b>(salen)H<sub>2</sub></b> , <sup>a</sup> ~1.0 g <sup>b</sup> in a vial	R36/37/38	S26 S28A S37 S37/39 S45
<b>Mn(OOCCH<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O</b> , ~1.9 g <sup>b</sup> in a vial	R36/37/38 R62 R63	S26 S37/39
<b>Lithium chloride solution</b> , LiCl, 1M solution in ethanol, 12 mL in a bottle	R11 R36/38	S9 S16 S26
<b>Ethanol</b> , 70 mL in a bottle	R11	S7 S16
Acetone, <b>(CH<sub>3</sub>)<sub>2</sub>CO</b> , 100 mL in a bottle	R11 R36 R66 R67	S9 S16 S26
<b>(salen*)MnCl<sub>x</sub></b> , <sup>c</sup> ~32 mL of a ~3.5 mg/mL <sup>b</sup> solution in a bottle		
KI <sub>3</sub> , ~0.010 M solution in water, <sup>b</sup> 50 mL in a bottle, labeled “ <b>I<sub>2</sub></b> ”.		
<b>Ascorbic Acid</b> , ~0.030 M solution in water, <sup>b</sup> 20 mL in a bottle		
<b>1% Starch</b> , solution in water, 2 mL in a bottle		
<b>TLC plate</b> – one 5 cm × 10 cm silica gel strip in a plastic zipper bag		

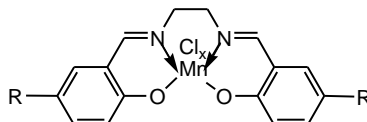
<sup>+</sup> See page 15 for definition of Risk and Safety Phrases.

<sup>a</sup> (salen)H<sub>2</sub>:



<sup>b</sup> The exact value is indicated on the label.

<sup>c</sup> (salen\*)MnCl<sub>x</sub> (both R groups are equal and can be either H, or COOH or SO<sub>3</sub>H):



Name:

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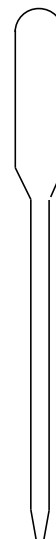
**Equipment**

**Common Use:** Balance

- Two **stands** with **clamps** located under hood labeled with your code
- One **hotplate stirrer**
- One **300 mm ruler**
- One **pencil**

**Kit #2:**

- Two **250 mL Erlenmeyer flasks** (one for synthesis, one for crystallization)
- One **graduated cylinder**, 50 mL
- One **20 mm long egg-shaped magnetic stirring bar**
- One **Hirsch funnel** (for suction filtration)
- **Filter paper** circles for Hirsch funnel and for TLC chamber
- One **125 mL suction flask for vacuum filtration**
- **Rubber adapter** for suction flask
- One 0.5 L **plastic ice bath**
- One **glass rod**
- Two 1 mL plastic transfer pipettes (see drawing in the right)
- One plastic spatula
- One empty **4 mL snap-cap vial** labeled “Product” for reaction product



**Kit #3:**

- Three empty **small screw-cap vials** (for TLC solutions)
- Ten **short capillary tubes (100 mm)** for TLC spotters
- One **watch glass** (for the TLC chamber)
- One **250 mL beaker** for TLC chamber

**Kit #4:**

- One assembled and ready to used **25 mL burette**
- One small **plastic funnel**
- Four **125 mL Erlenmeyer flasks**
- One **rubber bulb for pipettes**
- One **10 mL volumetric pipette**
- One **5 mL volumetric pipette**

**Name:**

**Code: TJK**

## **Risk and Safety Phrases (Task 2)**

R11 Highly flammable

R36/37/38 Irritating to eyes, respiratory system and skin

R62 Possible risk of impaired fertility

R63 Possible risk of harm to the unborn child

R66 Repeated exposure may cause skin dryness or cracking

R67 Vapors may cause drowsiness and dizziness

S7 Keep container tightly closed

S9 Keep container in a well-ventilated place

S16 Keep away from sources of ignition

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S28A After contact with skin, wash immediately with plenty of water.

S37 Wear suitable gloves.

S37/39 Wear suitable gloves and eye/face protection.

S45 In case of accident or if you feel unwell, seek medical advice immediately



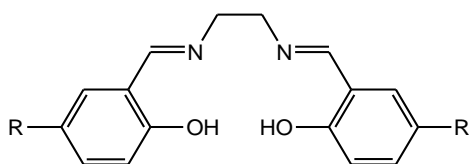
Name:

Code: TJK

**Task 2****22% of the Total****Synthesis of a Salen Manganese Complex and Determining Formula of the Product**

A	B-i	B-ii	C-i	C-ii	Task 2	22%
10	15	4	4	2	35	

Transition metal complexes of the 3d-block elements derived from the bis(salicylidene)ethylenediamine (salen) ligand have proven to be efficient catalysts of various redox reactions in organic synthesis.



**(salen)H<sub>2</sub>**, R = H

**(salen\*)H<sub>2</sub>**, R = H, COOH, or SO<sub>3</sub>H

The ability of the salen ligand to stabilize higher oxidation states of 3d-block elements is important in this chemistry. In particular, compounds of manganese in oxidation states from **+2 to +5** could be generated depending on the reaction conditions when the manganese salen complex is prepared. In this task you are required to prepare a manganese salen complex by reacting (salen)H<sub>2</sub> with Mn(II) acetate in ethanol in the air in the presence of lithium chloride. Under these conditions, you might have obtained a complex of the formula (salen)MnCl<sub>x</sub>, where **x = 0, 1, 2, or 3**.

You will need to:

- determine the mass of the product,
- characterize the purity of the material prepared using thin-layer chromatography (TLC),
- determine the metal oxidation state in the complex using an iodometric redox titration.

For the redox titration, you will be given a solution of a previously prepared analogue of your compound, (salen\*)MnCl<sub>x</sub>, where manganese has the same oxidation state as in the product and the R-substituent on the benzene ring is either H, COOH, or SO<sub>3</sub>H.

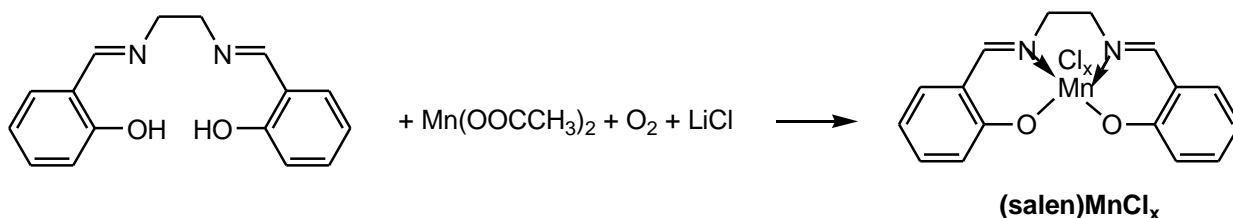
*Please read the whole description of this task and plan your work before you begin. Some operations have to be performed in parallel in order to complete it in time.*

Name:

Code: TJK

## Procedure:

### A. Synthesis of (salen)MnCl<sub>x</sub>



- 1) Place 2-3 crystals of **(salen)H<sub>2</sub>** aside in a small vial to be used for the TLC experiment later.
- 2) Transfer the pre-weighed ~1.0-g sample of **(salen)H<sub>2</sub>** provided into a 250 mL Erlenmeyer flask charged with a stirring bar. Add 35 mL of absolute ethanol to the reagent in the flask.
- 3) Place the flask on a hot plate/stirrer. Heat the contents with constant stirring until the solid dissolves (usually, dissolution is complete when the ethanol is about to boil). Then decrease the temperature setting to maintain the mixture close but **below its boiling point**. Do not boil the mixture so that the neck of the flask remains cool. If the flask is too hot to hold with bare hands, use a folded paper towel.
- 4) Remove the flask from the hotplate and add to its content a pre-weighed ~1.9-g sample of **Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O**. A dark brown color will develop. Return the flask to the hotplate immediately; continue heating and stirring for **15 min**. Do not boil the mixture so that the neck of the flask remains cool.
- 5) Remove the flask from the hotplate and add to its contents the provided solution of 1M **LiCl** in ethanol (12 mL, an excess). Return the flask to the hotplate; continue heating and stirring for **10 min**. Do not boil the mixture so that the neck of the flask remains cool.
- 6) After this time remove the flask from the hotplate, and place it in an ice bath for crystallization for **30 min**. Every 5 min gently scratch the walls of the flask from inside under the liquid level with a glass rod to accelerate crystallization of (salen)MnCl<sub>x</sub>. The first crystals may appear immediately upon cooling or after a period of only 10-15 minutes.
- 7) Use vacuum line located inside the hood (the corresponding valve is labeled “Vacuum”) and suction filter the crystalline solid formed using the small Hirsch funnel and a suction flask. Use a transfer pipette to **wash** the solid with few drops of **acetone** without disconnecting the flask from the vacuum line, and leave it on the filter (with the suction on) for **10-15 min** to air-dry.
- 8) Transfer the solid product into a **pre-weighed** vial labeled “Product”, then determine and record its mass,  $m_p$ , in the box below. Record also the mass of the following reagents used in the synthesis: (salen)H<sub>2</sub>,  $m_s$ , and Mn(OOCCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O,  $m_{Mn}$ .
- 9) Place the labeled vial with product into a zipper bag.

Name:

Code: TJK

Mass of the empty vial for the product: \_\_\_\_\_ g

Mass of the vial with the dried product: \_\_\_\_\_ g

Mass of the product,  $m_p$ : \_\_\_\_\_ g

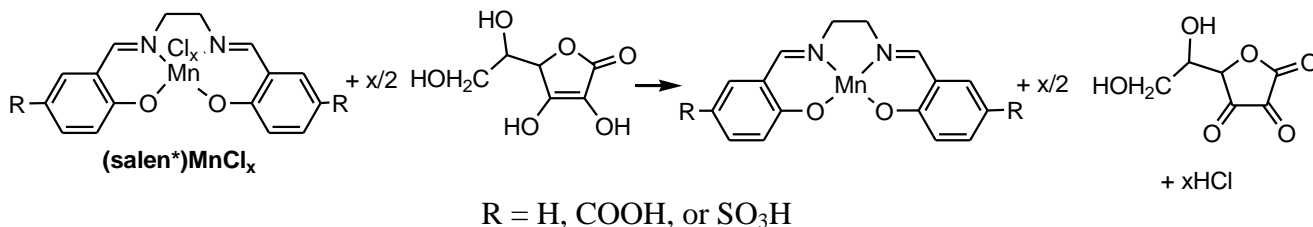
Mass of (salen)H<sub>2</sub> from label on the vial (copy from the label),  $m_S$ :  
\_\_\_\_\_ g

Mass of Mn(OOCCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O from label on the vial (copy from the label),  $m_{Mn}$ :  
\_\_\_\_\_ g

Name:

Code: TJK

**B. Volumetric analysis of a sample of (salen\*)MnCl<sub>x</sub> provided**



**How to use squeeze rubber bulb**

- Attach the bulb to a pipette
- Squeeze firmly the rubber bulb
- Squeeze the up arrow button to suck in some solution into pipette attached
- Squeeze the down arrow button to release some solution from the pipette into a target flask

**Note:** The pipettes and burette are ready to use and need not be conditioned.

- 1) Dispense 10.00 mL of the provided **(salen\*)MnCl<sub>x</sub> solution** into a 125 mL Erlenmeyer flask using the volumetric pipette.
- 2) Add 5.00 mL of the **ascorbic acid solution** to this solution and mix well. Allow the solution to stand for 3-4 minutes.
- 3) To avoid oxidation of ascorbic acid with O<sub>2</sub> do not delay and titrate the solution immediately with the **KI<sub>3</sub> solution** using 5 drops of a **1% starch** solution as indicator. The **blue or blue-green** endpoint should persist for at least 30 sec.
- 4) If time permits, perform 1-2 replicate titrations to improve the accuracy of your determination.

Place results of your titration experiment(s) in the table below:

#	Initial volume reading in burette of KI <sub>3</sub> solution, mL	Final volume reading in burette of KI <sub>3</sub> solution, mL	Volume of KI <sub>3</sub> solution consumed, mL
1			
2			
3			

**Name:**

**Code: TJK**

i. Indicate the volume (selected or averaged) of  $\text{KI}_3$  solution consumed in mL that you will use for calculations of molar mass of  $(\text{salen}^*)\text{MnCl}_x$  :

Volume of  $\text{KI}_3$  solution used in calculations: \_\_\_\_\_ mL

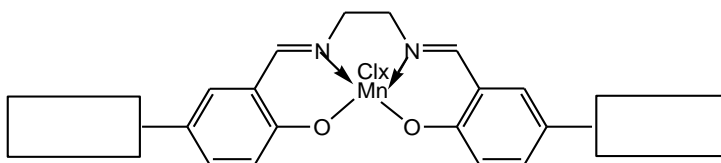
Concentration of  $(\text{salen}^*)\text{MnCl}_x$  (from label on the bottle): \_\_\_\_\_ mg/mL

Concentration of ascorbic acid (from label on the bottle): \_\_\_\_\_ M

Name:

Code: TJK

ii. From your titration data and referring to the table below deduce the value of  $x$ , the oxidation state of manganese and the identity of the substituent on the salen ligand ( $R = H, COOH, SO_3H$ ). Show them in the template below:



$x =$  \_\_\_\_\_

Manganese oxidation state: \_\_\_\_\_

R	$x$	(Theoretical molar mass)/ $x$ , g/mol
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240
COOH	3	172
SO <sub>3</sub> H	1	517
SO <sub>3</sub> H	2	276
SO <sub>3</sub> H	3	196

Name:

Code: TJK

**C. TLC characterization of (salen)MnCl<sub>x</sub>**

- 1) Dissolve a few crystals of the (salen)MnCl<sub>x</sub> (product) that you have prepared in a few drops of absolute ethanol using a small vial and a plastic transfer pipette for ethanol.
- 2) Dissolve a few crystals of (salen)H<sub>2</sub> in few drops of absolute ethanol using another small vial.
- 3) If necessary, use scissors (available from lab assistant upon request) to trim the TLC plate so it is an appropriate height for the TLC chamber.
- 4) Fold or cut a large circle of filter paper, and place it in the beaker so that it takes almost the full height of the beaker. This is required to saturate the chamber with ethanol vapor. Add ethanol to the beaker to wet the filter, and cover the bottom with a 3-4 mm thick layer of the solvent. Close the beaker with watch glass.
- 5) Mark the start.
- 6) Using the capillary tubes provided spot the TLC plate with **both solutions**.
- 7) Run a TLC in the beaker covered with a watch glass for 10-15 min.
- 8) Mark the solvent front as well as the colored spots on the TLC plate using a pencil.
- 9) Dry the TLC plate in air and place it back into a zipper bag.
- 10) Calculate the  $R_f$  for both (salen)H<sub>2</sub> and (salen)MnCl<sub>x</sub>.

Name:

Code: TJK

i. Sketch the TLC plate on your answer sheet

ii. Determine and record the  $R_f$  values for (salen) $\text{H}_2$  and (salen) $\text{MnCl}_x$

$R_f$ , (salen) $\text{H}_2$ : \_\_\_\_\_

$R_f$ , (salen) $\text{MnCl}_x$ : \_\_\_\_\_

When you are finished working:

- Place liquid wastes into a container marked **Liquid Waste**.
- Place used vials into a contained labeled **Broken Glass Disposal**.
- Place used glassware back to appropriate boxes labeled “Kit #2”, “Kit #3” and “Kit #4”.