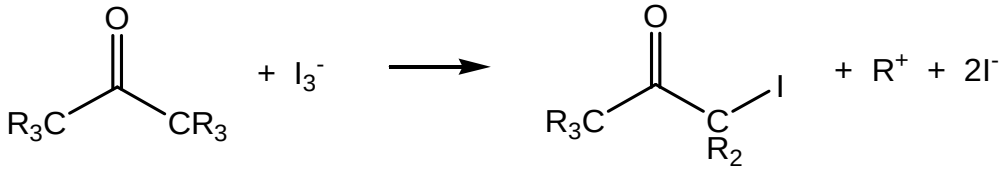
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

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 impart 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:



R = H or D

The reaction takes place with a rate law

$$\text{Rate} = k\,[\text{acetone}]^m\,[I_3^-]^n\,[H^+]^p$$

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 You will also compare the reactivity of acetone with that of acetone-d_6, where the six atoms of protium (^{1}H) have been replaced by deuterium (^{2}H, D), to determine the isotope effect (k_H / k_D) of the reaction.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.

Chemicals

- HCl, aqueous solution, c = ~2 mol dm^{-3} ***)**, 50 cm^3
- KI_3, aqueous solution, c = ~0.01 mol dm^{-3} ***)**, 10 cm^3 , labelled "I_2",
- Acetone, $(CH_3)_2CO$, M = 58.08 g mol^{-1}, density = 0.791 g cm^{-3}, 10 cm^3,

- Acetone-d_6, $(CD_3)_2CO$, M = 64.12 g mol^{-1}, density = 0.872 g cm^{-3}, 3.0 cm^3

_____

*) The exact concentration is indicated on the label.

Procedure

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

Measure the volumes of hydrochloric acid, distilled water, and potassium triiodide solution (labelled as "I_2") 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):

$[H^+]$: between 0.2 and 1.0 mol dm^{-3}

$[I_3^-]$: between 0.0005 and 0.002 mol dm^{-3}

[acetone]: between 0.5 and 1.5 mol dm^{-3}

To initiate the reaction, add the chosen volume of acetone to the solution containing the other reagents, quickly cap 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 table 1.1. 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 colour of the triiodide ion. Record the time required for the colour to disappear. When the reaction is complete, set aside the vessel, and leave it sealed so that you do not expose yourself to iodoacetone vapours.

Repeat as often as desired with different concentrations of reagents. Report the concentrations of the reagents that you use in table 1.3.

Hint: Change one concentration at a time.

Once 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 cm^3 of acetone-d_6 because of the greater expense of the isotopically labelled 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 ampoule 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 have finished your work:

a) empty the water bottle and place it along with any unused equipment back to the box labelled “Kit #1”,

b) place used pipettes and sealed used vials in designated containers under the hoods,

c) use a container labelled “Broken Glass Disposal” to dispose of all parts of the empty ampoule.

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

1.1 Record your results for acetone, $(CH_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.1

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CH_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1					
2					
3					
etc.					

1.2 Record your results for acetone-d_6, $(CD_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.2

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CD_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1d					
2d					
3d					
etc.					

1.3 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 1.5 and 1.6), but you must indicate which run or runs you used in your calculation by checking the appropriate box in the right-hand column.

Table 1.3

$(CH_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CH_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_H? **Yes**	**No**
1					❑	❑
2					❑	❑
3					❑	❑
etc.						

Table 1.4

$(CD_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CD_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_D? **Yes**	**No**
1d					❑	❑
2d					❑	❑
3d					❑	❑

1.4 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 =

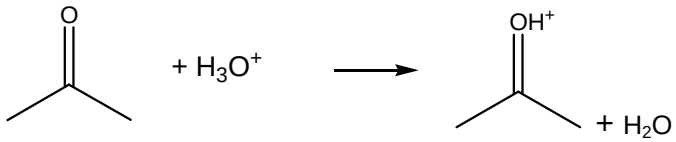
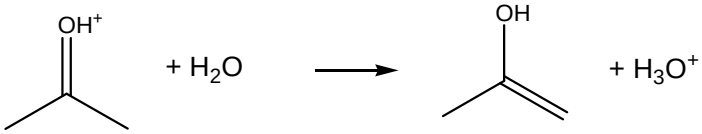
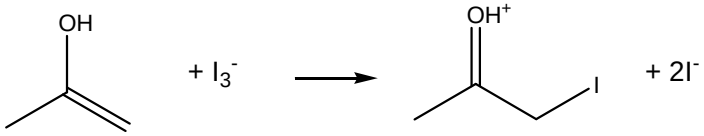
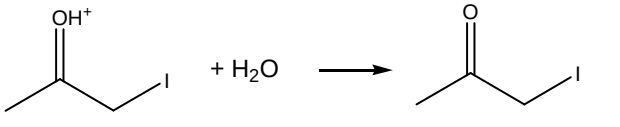
1.5 Calculate the rate constant k_H for the reaction of acetone, $(CH_3)_2CO$, and indicate the units.

1.6 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).

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 with all previous steps rapidly achieving an equilibrium that strongly favours the reactants.

1.7 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 **1.4**) is **consistent** with that step being rate-determining and a mark (**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 1.6) is **consistent** with that step being rate-determining and a mark **X** if your measured isotope effect is **inconsistent** with that step being rate-determining.

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
		
		
		
		

SOLUTION

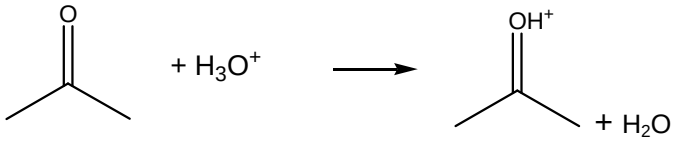
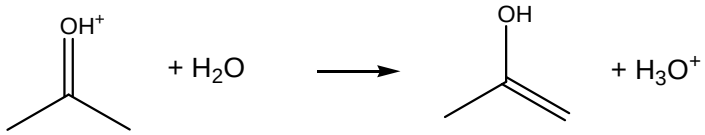
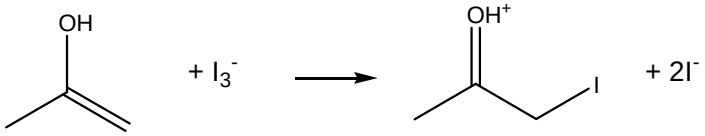
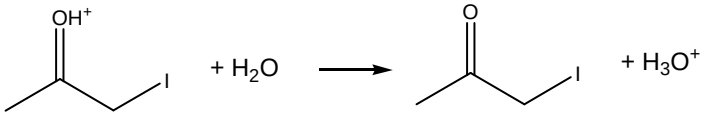
1.4 m = 1; n = 0; p = 1

1.5 $k_H = 2.8 \pm 0.4 \cdot 10^{-5}$ dm^3 mol^{-1} s^{-1}

1.6 $k_D = 4.3 \pm 0.6 \cdot 10^{-6}$ dm^3 mol^{-1} s^{-1}

$k_H / k_D = 6.5 \pm 0.4$

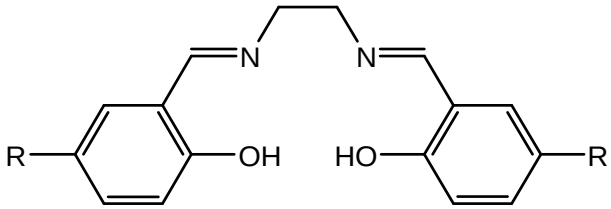
1.7

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
	✓	**X**
	✓	✓
	**X**	**X**
	**X**	**X**

PROBLEM 2 (Practical)

Synthesis of a Salen Manganese Complex and Determining Formula of the Product

Transition metal complexes of the 3*d*-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_2, R = H

(salen*)H_2, R = H, COOH, or SO_3H

The ability of the salen ligand to stabilize higher oxidation states of 3*d*-block elements is important in this sphere of chemistry. In particular, compounds of manganese in oxidation states from II to V 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_2 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)$MnCl_x$, where x = 0, 1, 2, or 3.

You are expected to:

i) determine the mass of the product,

ii) characterize the purity of the material prepared using thin-layer chromatography (TLC),

iii) determine the metal oxidation state in the complex using an iodometric redox titration.

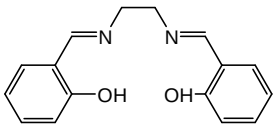
For the redox titration, you will be given a solution of a previously prepared analogue of your compound, (salen*)$MnCl_x$, where manganese has the same oxidation state as in the product and the substituent R on the benzene ring is either H, COOH, or SO_3H.

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.

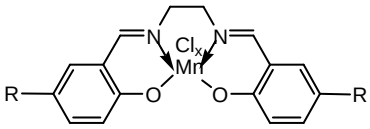
Chemicals

Note: The exact values of masses and concentrations of the particular chemicals are indicated on the labels.

- **(salen)H_2**, ~1.0 g in a vial



- $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, ~1.9 g in a vial
- Lithium chloride, solution in ethanol, c = 1 mol dm^{-3}
- Ethanol
- Acetone
- (salen*)$MnCl_x$, ~32 cm^3 of a solution with a mass concentration of ~3.5 mg cm^{-3}



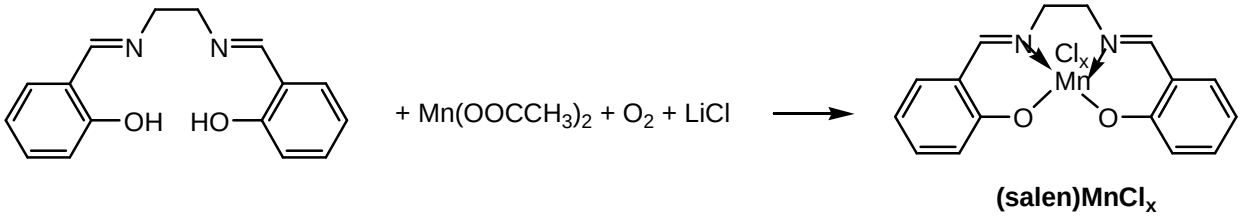
Both R groups are equal and can be either H, or COOH or SO_3H.

- KI_3, 50 cm^3 of an aqueous solution in a bottle, labelled "I_2", c = ~0.010 mol dm^{-3}.
- Ascorbic acid, 20 cm^3 of an aqueous solution, c = ~0.030 mol dm^{-3}.
- Starch, w = 0.01, 2 cm^3 solution in water,

Procedure:

A. Synthesis of (salen)$MnCl_x$

B.



(salen)$MnCl_x$

(1) Place 2-3 crystals of (salen)H_2 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_2 provided into a 250 cm^3 Erlenmeyer flask charged with a stirring bar. Combine the reagent with 35 cm^3 of absolute ethanol.

(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 $Mn(OAc)_2 \cdot 4\ H_2O$. A dark brown colour will develop. Return the flask to the hotplate immediately and 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 LiCl (c = 1 mol dm^{-3}) in ethanol (12 cm^3, an excess). Return the flask to the hotplate and 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)$MnCl_x$. 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 labelled “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 labelled “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_2, m_S, and $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, m_{Mn}.

(9) Place the labelled vial with product into a zipper bag.

You are required to fill in the following table:

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

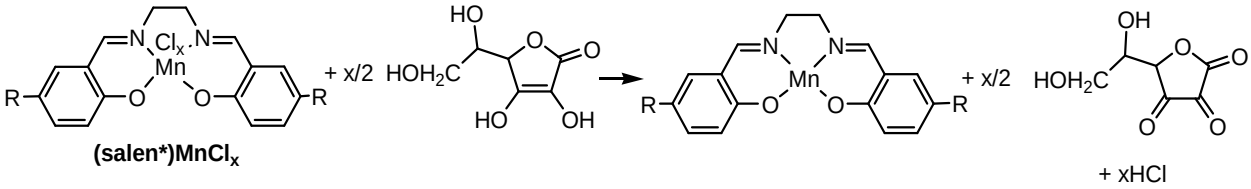
Mass of (salen)H_2 from label on the vial (copy from the label), m_S:

_____ g

Mass of $Mn(OOCCH_3)_2 \cdot 4\ H_2O$ from label on the vial (copy from the label), m_{Mn}:

_____ g

B. Volumetric analysis of a sample of (salen*)$MnCl_x$ provided



(salen*)$MnCl_x$

R = H, COOH, or SO_3H

Procedure:

(1) Dispense 10.00 cm^3 of the provided (salen*)$MnCl_x$ solution into a 125 cm^3 Erlenmeyer flask using the volumetric pipette.

(2) Add 5.00 cm^3 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_2 do not delay and titrate the solution immediately with the KI_3 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 table 2.1.

Table 2.1. Results of the titration experiment(s).

#	Initial volume reading in burette of KI_3 solution, cm^3	Final volume reading in burette of KI_3 solution, cm^3	Volume of KI_3 solution consumed, cm^3
1			
2			

_____

2.1 Indicate the volume (selected or averaged) of KI_3 solution consumed in cm^3 that you will use for calculations of molar mass of (salen*)$MnCl_x$.

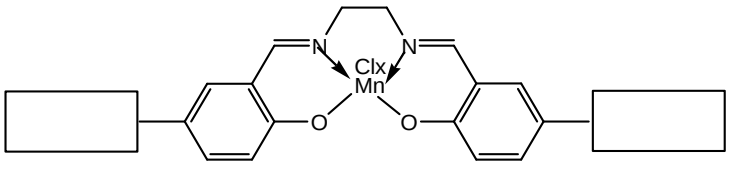
Concentrations of (salen*)$MnCl_x$ (in mg cm^{-3}) and ascorbic acid (in mol dm^{-3}) are given on the labels of the particular bottles.

2.2 From your titration data and referring to the table 2.2 deduce:

i) the value of *x*,

ii) oxidation state of manganese,

iii) the identity of the substituent on the salen ligand (R = H, COOH, SO_3H). Show them in the template below.



x = _____

Manganese oxidation state: _____

Table 2.2

R	x	(Theoretical molar mass)/x, g mol^{-1}
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240

Table 2.2 continued

COOH	3	172
SO_3H	1	517
SO_3H	2	276
SO_3H	3	196

C. TLC characterization of (salen)$MnCl_x$

(1) Dissolve a few crystals of the (salen)$MnCl_x$ 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_2 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 trim 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 vapour. 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 coloured spots on the TLC plate using a pencil.

(9) Dry the TLC plate in air and place it back into a zipper bag.

———

2.3 Calculate the R_f for both (salen)H_2 and (salen)$MnCl_x$.

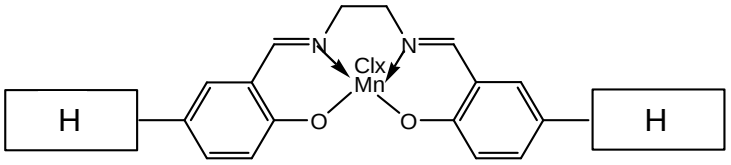
2.4 Sketch the TLC plate on your answer sheet.

2.5 Determine and record the R_f values for (salen)H_2 and (salen)$MnCl_x$.

———————————

SOLUTION

2.2



x = 1

Manganese oxidation state: 3

2.4 Evaluation of the TLC plate:

Maximum points:

- for the appearance of two spots on the start line,
- for the start and solvent front lines,
- for the clearly visible spots.

2.5 The relevant R_F values:

Compound	R_f
(salen)H_2	0.58 – 0.68
(salen)$MnCl_x$	0.30 – 0.40