PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+.

$$CH_3\text{-}CO\text{-}CH_3\ (aq) + I_2\ (aq) \xrightarrow{H^+} CH_3\text{-}CO\text{-}CH_2I\ (aq) + H^+(aq) + I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of I_2(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$\text{Initial rate} = k\,[CH_3COCH_3]_0^x\,[I_2]_0^y\,[H^+]_0^z$$

where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H^+, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the I_2(aq) concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1. Aqueous iodine solution in 0.4 M KI 80 cm^3
2. 0.100 M aq. HCl 50 cm^3
3. 0.50 M aq. CH_3COONa 80 cm^3
4. Standard 0.02 M $Na_2S_2O_3$(aq) solution 200 cm^3
   (the exact concentration will be announced at the beginning of practical part)
5. Aqueous acetone (50% by volume) 50 cm^3
   (Density of pure acetone; 0.787 g cm^{-3}, MW. = 58.08)
6. Starch indicator 7 cm^3

Procedure

A. Standardization of Iodine Solution

1. Pipet 5.00 cm^3 of aqueous iodine into a clean 125 cm^3 Erlenmeyer flask.
2. Add 10 cm^3 of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm^3)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

3. Measure out 10 cm^3 of 0.50 M aq. CH_3COONa into the graduated cylinder.
4. Set the stop-watch to 0.0000 display.
5. Pipet 5.00 cm^3 of iodine solution into the stoppered Flask No. I.
   Start the stop-watch as soon as the first drop of iodine solution is added.
6. Stopper the flask and swirl continuously.
7. Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm^3 of sodium acetate solution (from step 3) into the reaction flask. Shake well.
8. Titrate the remaining iodine with standard thiosulphate solution.
9. Record the volume of the thiosulphate solution.
10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

    Flask II: 10.00 cm^3 I_2 solution
    Flask III: 5.00 cm^3 I_2 solution
    Flask IV: 5.00 cm^3 I_2 solution

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in M s^{-1}.

B-4. The rate of reaction has the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $Na_2S_2O_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV*.

$$\text{Rate of disappearance of iodine (M s}^{-1}) = -\frac{d[I_2]}{dt} = \frac{c(I_2)_{\text{initial}} - c(I_2)_{7\,\text{min}}}{7 \times 60\ s}$$

B-4. *Calculation of x, y, and z in the rate equation*:

$$\text{rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

In comparing the rates in solutions **II** : **I**, **III** : **I**, and **IV** : **I** one can calculate the following values:

x = 1; y = 0; z = 1

The rate equation has the form: rate = $k\,[CH_3COCH_3]\,[H^+]$

B-5. *Calculation of the rate constants for solution mixtures **I** to **IV** and the mean value of the rate constant.*

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH_3, 5 % aq. $AgNO_3$, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. $NaHCO_3$, 1 % $FeCl_3$ in EtOH, 0.2 % aq. $KMnO_4$, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm^3 round bottomed flask for distillation and a 10 cm^3 round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm^3 of water in the 25 cm^3 round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm^3 of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm^3 capped centrifuge tube and add 1 cm^3 of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm^3 test tube. Repeat this extraction with fresh 1 cm^3 dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm^3 conical vial. Use approximately 1 cm^3 of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm^3. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm^3) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. $AgNO_3$ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^{1}H NMR spectra. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

4. Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.

5. Draw the structures of compound X and unknown Y. Assign each proton of unknown **Y** from the provided ^{1}H NMR spectra in the same manner as in (4).

SOLUTION

1. It was expected to obtain at least 5 cm^3 of distillate.

2. Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % $KMnO_4$	✓	
1 % $FeCl_3$	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

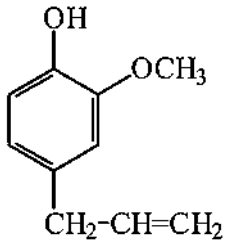
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

3. Funcional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % $NaHCO_3$	✓	
0.2 % $KMnO_4$		✓
1 % $FeCl_3$		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

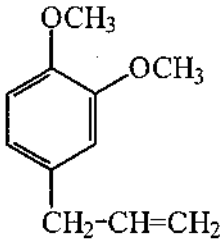
Functional groups in **Unknown Y**	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

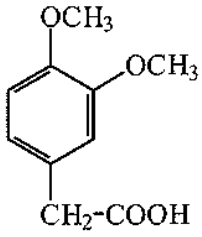


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

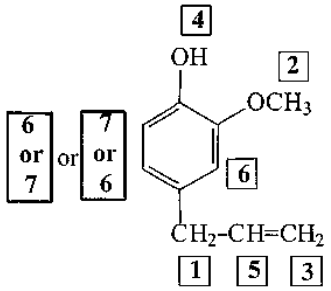


NMR spectrum of the main essential oil (S):

(See peak number in the given 'H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	S
3 4	5.0 – 5.1	2H	m
5	5.6	1H	S
	5.9 – 6.0	1H	m
6	6.7	2H	S d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):



NMR spectrum of the unknown **Y**:

(See peak number in the given 'H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):

