National Examination for 2013 IChO

Taiwan

Round 4 Practical Examination (5 hours)

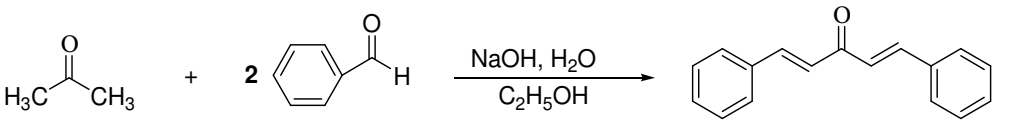
Task 1. Enolate Condensation: Synthesis of dibenzalacetone

A. Principle

The Claisen-Schmidt reaction involves the synthesis of aṇα,β-unsaturated ketone by the condensation of an aromatic aldehyde with a ketone. The aromatic aldehyde possesses no hydrogens α-to the carbonyl group, it cannot therefore undergo self condensation but reacts rapidly with the ketone present.

The initial aldol adduct cannot be isolated as it dehydrates readily under the reaction conditions to give an α,β-unsaturated ketone. This unsaturated ketone also possesses activated hydrogens α-to a carbonyl group and may condense with another molecule of the aldehyde.

In this experiment you will carry out the base catalysed aldol condensation of benzaldehyde with acetone. The product will be purified by recrystallization.



Acetone
molar mass: 58 g/mol
density: 0.79g/mL
limiting reagent

Benzaldehyde
molar mass: 106 g/mol
density: 1.04 g/mL
an excess will be used

Dibenzalacetone
(1,5-diphenyl-1,4-pentadien-3-one)
molar mass: 234 g/mol

B. Reagents

acetone, benzaldehyde, 95% alcohol, NaOH solution (3 M), ethylacetate, and hexanes.

C. Equipments

Test tube (15 x 2 cm), test tube rack, test tube clamp, septum, beaker (100 mL), graduate cylinder (10 mL), droppe, watch glass, spatular, syringe and needle (1 mL), microcentifuge tube (1.5 mL), TLC and TLC chamber.

Hot water: 60℃, vacuum filtration, filter paper and funnel, melting point instrument.

D. Procedure

Notice: benzaldehyde should not be more than 2 equivalents.

1. Take 4 mL 3 M NaOH solution and 3.2 mL of 95 % ethanol into large test tube, mix well.
2. Add 0.5 mL of benzaldehyde, and then 0.15 mL of acetone into the test tube. Use septum to stop the test tube to avoid vaporization of acetone.

3. Shake the test tube to mix solution. Hold the septum to prevent gas leak out. Continuously shake the test tube. Yellow solid will form in about 3~5 min. Shake the test tube occasionally for about 15 min. Collect the solid by vacuum filtration. Wash the solid with water.
4. Transfer the solid into a small test tube, and pour in 4 mL of 95% ethanol. Use test tube clamp and put the test tube in 60℃ water bath until all solid dislove.
5. Take the test tube out and cool to room temperature. Leave the test tube on ice bath for about 15 min to crystallize.
6. Weight out a filter paper then do vacuum filtration. Wash the solid with small amount of ice cold ethanol.
7. Transfer the filter paper with the yellow products onto a watch glass and put it into 50℃ oven for drying.
8. Weight out the products, calculate the yield. Measure melting point.
9. Take small amount of product into microcentifuge tube. Disolve it in ethylacetate and run TLC. Use hexanes:ethylacetate = 10:1 to elude the TLC. Calculate R_f.

Task 2. Quantitative analysis of Ascorbic Acid in Vitamin *C* Tablet

The main component of over-the-counter vitamin *c* tablet is ascorbic acid (MW=176.12). It is an acid and a reductant. Both acid-base and redox titration can be employed to quantitatively determine the amount of ascribe acid.

This experiment has two parts, the first part is acid-base titration and the second part is redox titration. You are asked to give a command on these two types of titration in this application.

Your points are base on the accuracy of the amount of unknown sample. Error within 2 % gets full points. Error between 2 to 7 % will scale linearly to the full points. Error larger than 7 % gets no points.

Check your reagents and equipments before you start

Reagent	Equipment
$NaOH_{(aq)}$ 1 bottle (concentration shown on label) ~0.01 M $I_{2(aq)}$ 1 bottle (concentration shown on label) Indicator phenolphthalein methyl red starch	Calculator 1 ea Graduated cyclinder： 50 mL 1 ea 10 mL 1 ea Erlenmeyer： 125 mL 5 ea Beaker： 1000 mL 1 ea 100 mL 3 ea
Miscellaneous	Volumnmetric： 100 mL 1 ea 25 mL 1 ea 10 mL 1 ea
Distilled water Kimwipe Detergent safety goggle 1 pair glove 1 pair napkin 1 ea	2 x 50 mL Burette and rack funnel 1 ea dropper 5 ea glass rod 1 ea

Procedure

1. Dissolve a tablet of Vitamin C provided into about 60 mL of water, then diluted to 100 mL precisely.

A: Acid-Base titration

1. Pipette 10 mL of the above Vitamin C solution into an Erlenmeyer flask. Add few drops of proper indicator before titrate with NaOH solution with known concentration.

2. Repeat step 1 at least three times. Take an average of the titrated volume.

B: Oxidation-reduction titration

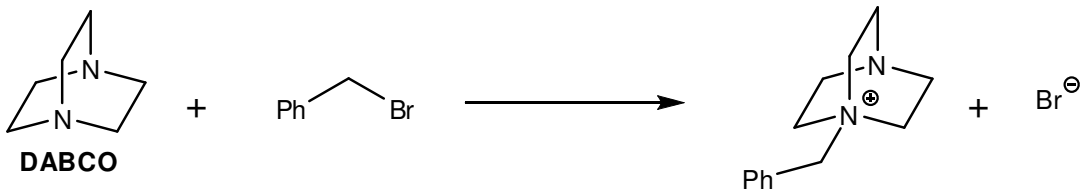
1. Pipette 10 mL of the above Vitamin C solution into an Erlenmeyer flask. Use standard iodine solution to titrate and use starch as indicator. The blue color must remain at least 15 seconds at the end of titration.

2. Repeat step 1 at least three times. Take an average of the titrated volume.

The solution provided in this experiment are all standardized with the concentration written on the reagent bottle. Use the given concentration for all calculation.。

Task 3. The Menshutkin Reaction

The nucleophilic substitution reaction between a tertiary amine and an alkyl halide is known as the Menshutkin reaction. This experiment investigates the rate law for the reaction between the amine known as DABCO (1,4-diazabicylo[2.2.2]octane) and benzyl bromide:



It is possible for the second nitrogen in the DABCO molecule to react with a second benzyl bromide. However, in this experiment the DABCO will always be in excess so further reaction is unlikely. The reaction could proceed by either the S_N1 or the S_N2 mechanism. In this experiment, you will confirm that the order with respect to benzyl bromide is 1 and determine the order with respect to DABCO. This should enable you to distinguish between the two possible mechanisms.

As the reaction proceeds neutral species, DABCO and benzyl bromide, are replaced by charged species, the quaternary ammonium ion and Br^-. Therefore the electrical conductivity of the reaction mixture increases as the reaction proceeds and so the progress of the reaction can be followed by measuring the electrical conductivity as a function of time.

Benzyl bromide is a lacrymator. This experiment should be performed in a fume hood.

The Method in Principle

The rate law for the reaction can be written as

$$\frac{\mathrm{d}[\mathrm{Br}^-]}{\mathrm{d}t} = k[\mathrm{RBr}][\mathrm{DABCO}]^{\alpha} \qquad [1]$$

where we have assumed that the order with respect to the benzyl bromide, RBr, is 1 and the order with respect to DABCO is α.

In the experiment, the concentration of DABCO is in excess and so does not change significantly during the course of the reaction. The term $k[\mathrm{DABCO}]^{\alpha}$ on the right-hand side of Eqn. [1] is thus effectively a constant and so the rate law can be written

$$\frac{\mathrm{d}[\mathrm{Br}^-]}{\mathrm{d}t} = k_{\mathrm{app}}[\mathrm{RBr}] \quad \text{where} \quad k_{\mathrm{app}} = k[\mathrm{DABCO}]^{\alpha} \qquad [2]$$

k_{app} is the apparent first order rate constant under these conditions; it is not really a rate "constant",

as it depends on the concentration of DABCO.

To find the order with respect to DABCO we measure k_{app} for reaction mixtures with different excess concentrations of DABCO. From Eqn. [2], and taking logs, we find

$$\ln k_{app} = \ln k + \alpha \ln[\text{DABCO}] \qquad [3]$$

So a plot of ln k_{app} against ln [DABCO] should give a straight line of slope α.

k_{app} may be found by measuring the conductance at time t, $G(t)$, and at time infinity, G_∞. In the supplementary material it is shown that a graph of $\ln[G_\infty - G(t)]$ against t should be a straight line with slope k_{app}.

In practice it is rather inconvenient to measure conductance at time infinity but this can be avoided by analysing the data using the *Guggenheim method.* In this method each reading of the conductance at time t, is paired up with another at time $t + \Delta$, $G(t+\Delta)$, where Δ is a fixed time interval that needs to be at least a half-life. As shown in the supplementary material, a plot of $\ln[G(t+\Delta)-G(t)]$ against time should be a straight line of slope $-k_{app}$. For example, suppose we take measurements at fixed regular intervals, say each 30 s and choose an appropriate value of Δ, say 3 minutes (180 s). The plot made is of the points $\{x,y\} = \{0, \ln[G(180)-G(0)]\}$, $\{30, \ln[G(210)-G(30)]\}$, $\{60, \ln[G(240)-G(60)]\}$, ...

The Apparatus

Cheap conductivity meters are commercially available, for example the Primo5 conductivity stick meter from Hanna instruments works well with this practical. These simply dip into the solution and the conductance of the solution can be read off the digital display.

Procedure

You are provided with the following solutions, all in ethanol: 0.15, 0.20 and 0.25 mol dm^{-3} DABCO, and approx. 0.6 mol dm^{-3} benzyl bromide (this must be freshly made up). You should measure k_{app} for each of these solutions by measuring the conductance as a function of time and then analysing the data using the Guggenheim method. From the three values of k_{app}, the order with respect to DABCO can be found by plotting ln k_{app} against ln [DABCO], as shown by Eqn. [3].

Ideally we ought to keep the reagents and the reaction mixture in a thermostat. However, as the heat evolved is rather small, the temperature will remain sufficiently constant for our purposes.

Kinetic Runs

1. Rinse the conductivity dipping electrode with ethanol from a wash bottle, catching the waste in a beaker. Allow the excess ethanol to drain off and gently dry the electrode with tissue.
2. Transfer 10 cm^3 of the DABCO solution to a clean dry boiling tube.
3. Add 100 µl of the benzyl bromide solution.
4. Insert and withdraw the dipping electrode of the conductance meter a few times in order to mix

the solution and then, with the electrode in place, start the stop-watch.

5. Record the conductance at 30 second intervals (it is essential to make the measurements at regular intervals), starting with the first reading at 30 seconds and continuing until there is no further significant change in the conductance, or for 10 minutes, whichever is the shorter time.

6. *From time to time*, *gently* lift the electrode in and out so as to stir the solution.

7. Once the measurements have been made, remove the electrode, discard the solution and clean the electrode as in step 1.

8. Make the measurements for the 0.15 mol dm^{-3} solution of DABCO, and then for the 0.20 and 0.25 mol dm^{-3} solutions.

Data Analysis

For each run determine k_{app} using the Guggenheim method – three minutes is about right for the fixed interval Δ. Then plot ln k_{app} against ln [DABCO] and hence determine the order with respect to DABCO.

Supplementary information

The key to this experiment is how to use the measured conductance of the reaction mixture to determine the first order rate constant, k_{app}. The first stage is simply to integrate the rate law; to do this we note that for each benzyl bromide molecule that reacts one bromide ion is generated so that at any time $[Br^-] = [RBr]_{init} - [RBr]$, where $[RBr]_{init}$ is the initial concentration of benzyl bromide. Thus the rate equation can be written in terms of $[Br^-]$ by putting $[RBr] = [RBr]_{init} - [Br^-]$; integration is then straightforward:

$$\frac{d[Br^-]}{dt} = k_{app}\left([RBr]_{init} - [Br^-]\right)$$

$$\int \frac{d[Br^-]}{\left([RBr]_{init} - [Br^-]\right)} = \int k_{app}\,dt$$

i.e. $$-\ln\left([RBr]_{init} - [Br^-]\right) = k_{app}t + \text{const.}$$

The constant can be found by saying that at time zero, $[Br^-] = 0$, hence

$$-\ln\left([RBr]_{init}\right) = \text{const.}$$

hence $$-\ln\left([RBr]_{init} - [Br^-]\right) = k_{app}t - \ln\left([RBr]_{init}\right)$$

which can be written

$$[Br^-] = [RBr]_{init}\left(1 - \exp[-k_{app}t]\right) \quad [4]$$

When the reaction has gone to completion, at time infinity, the concentration of bromide is equal to the initial concentration of RBr so Eqn. [4] can be written

$$[Br^-] = [Br^-]_\infty\left(1 - \exp[-k_{app}t]\right) \quad [5]$$

where $[Br^-]_\infty$ is the concentration of Br^- at time infinity. Equation [5] says that the concentration of Br^- approaches a limiting value of $[Br^-]_\infty$ with an exponential law. A similar relationship can be written for the other product, the quaternary ammonium ion, whose concentration will be written $[R_4Br^+]$.

$$[\mathrm{R_4Br^+}] = [\mathrm{R_4Br^+}]_\infty \left(1 - \exp[-k_{\mathrm{app}} t]\right) \quad [6]$$

We will assume that the conductance of the reaction mixture, G, is proportional to the concentration of the charged species present:

$$G = \lambda_{\mathrm{Br^-}}[\mathrm{Br^-}] + \lambda_{\mathrm{R_4N^+}}[\mathrm{R_4N^+}]$$

where λ are simply the constants of proportionality.

Using Eqns. [5] and [6] to substitute for the concentration of Br^- and R_4N^+ we find

$$\begin{aligned} G &= \lambda_{\mathrm{Br^-}} \left\{[\mathrm{Br-}]_\infty \left(1 - \exp[-k_{\mathrm{app}} t]\right)\right\} + \lambda_{\mathrm{R_4N^+}} \left\{[\mathrm{R_4Br^+}]_\infty \left(1 - \exp[-k_{\mathrm{app}} t]\right)\right\} \\ &= \left(\lambda_{\mathrm{Br^-}}[\mathrm{Br-}]_\infty + \lambda_{\mathrm{R_4N^+}}[\mathrm{R_4Br^+}]_\infty\right)\left(1 - \exp[-k_{\mathrm{app}} t]\right) \\ &= G_\infty \left(1 - \exp[-k_{\mathrm{app}} t]\right) \qquad [7] \end{aligned}$$

where we have recognised that $\left(\lambda_{\mathrm{Br^-}}[\mathrm{Br-}]_\infty + \lambda_{\mathrm{R_4N^+}}[\mathrm{R_4Br^+}]_\infty\right)$ is the conductance at time infinity, G_∞.

Equation [7] can be rearranged to give a straight line plot:

$$1 - \frac{G}{G_\infty} = \exp[-k_{\mathrm{app}} t]$$

$$\ln\left(1 - \frac{G}{G_\infty}\right) = -k_{\mathrm{app}} t \qquad \text{or} \qquad \ln\left(\frac{G_\infty - G}{G_\infty}\right) = -k_{\mathrm{app}} t$$

$$\text{or} \qquad \ln\left(G_\infty - G\right) = -k_{\mathrm{app}} t + \ln G_\infty$$

Hence a plot of $\ln\left(G_\infty - G\right)$ against t should be a straight line with slope k_{app}.

The Guggenheim Method

From Eqn. [9] the conductance at time t, $G(t)$, can be written

$$G(t) = G_\infty \left(1 - \exp[-k_{app} t]\right)$$

At some time ($t + \Delta$) later the conductance is $G(t + \Delta)$

$$G(t+\Delta) = G_\infty \left(1 - \exp[-k_{app}(t+\Delta)]\right)$$

The difference $G(t + \Delta) - G(t)$ is

$$G(t+\Delta) - G(t) = G_\infty \left(1 - \exp[-k_{app}(t+\Delta)] - 1 + \exp[-k_{app}t]\right)$$

$$= G_\infty \left(\exp[-k_{app}t] - \exp[-k_{app}(t+\Delta)]\right)$$

$$= G_\infty \exp[-k_{app}t]\left(1 - \exp[-k_{app}\Delta]\right)$$

Taking logarithms of both sides gives, from the last line,

$$\ln\left(G(t+\Delta) - G(t)\right) = \ln G_\infty - k_{app}t + \ln\left(1 - \exp[-k_{app}\Delta]\right)$$

This implies that a plot of $\ln\left(G(t+\Delta) - G(t)\right)$ against time should be a straight line of slope $-k_{app}$; to make this plot there is no need to know the value of the conductance at infinite time, G_∞, and this is the main advantage of the Guggenheim method.

Answer sheets

Task 1 (70 points)

Attach TLC

	product
	Dibenzalacetone
molecular weight	
# of mole	
theoretical weight (g)	
experimental weight (g)	filter paper:_____ g filter paper + product:_____ g product:_____ g
yield (50 pts)	%
melting point (10 pts)	°C
R_f (10 pts)	

Task 2 (100 points)

A: Acid-base titration (40 pts)

1st titration: sample _____mL, NaOH _____mL.

2nd titration: sample _____mL, NaOH _____mL.

3rd titration: sample _____mL, NaOH _____mL.

sample _____mL, NaOH _____mL.

sample _____mL, NaOH _____mL.

Average volume for NaOH solution _____mL。

B: Oxidation-reduction titration (40 pts)

1st titration: sample _____mL, NaOH _____mL.

2nd titration: sample _____mL, I_2 solution _____mL.

3rd titration: sample _____mL, I_2 solution _____mL.

sample _____mL, I_2 solution _____mL.

sample _____mL, I_2 solution _____mL.

Average volume for I_2 solution _____mL。

C: Calculation:： (4 pts for each question)

1. Assume ascorbic acid is a monoprotic acid, calculate the total amount of ascorbic acid in the Vitamin C tablet from acid-base titration.

2. Write down the balance equation of iodine and thiosulfate reaction.

3. Write down the balance equation of iodine and Vitamin C reaction.

4. Calculate the total amount of ascorbic acid in the Vitamin C tablet from both acid-base and redox titration.

D: Are the amount of ascorbic acid from two titrations the same? Why is that? Compare the two titration methods. List the advantage and disadvantage of both methods.

Task 3 (100 points)

1. Deduce $k_{app.}$。Two graphs for each concentration, one for experimental conductivity vs time and one for processed plot (They may be plotted on the same graph paper with clear label). Label concentration on each graph paper and write your name on it. (25 pts for each concentration)

[DABCO]	k_{app} (with unit)
0.15 M	
0.20 M	
0.25 M	

2. The order of DABCO in the rate law (need plot too). (15pts)

3. Write down the rate law and calculate the rate constant. (10 pts)