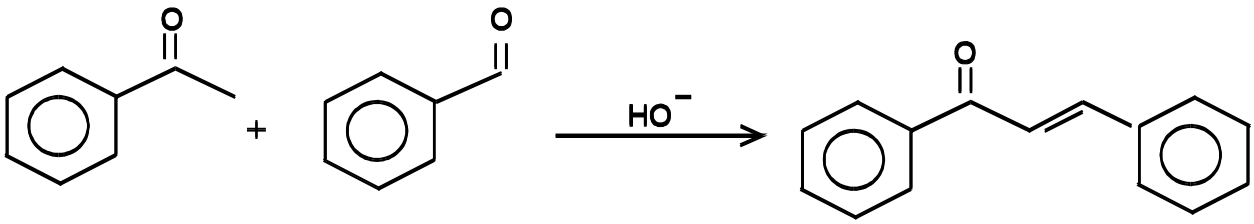
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis involving Carbanions Chalcone

The aim of this experiment is to condense acetophenone and benzaldehyde in a mixed aldol condensation. After spontaneous dehydratation, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.



a) *Starting the condensation reaction*

In a 250 cm^3 ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm^3 of water, then add slowly under stirring 20 cm^3 of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm^3) of acetophenone and 8.5 g (0.08 mol = 8.5 cm^3) of benzaldehyde. Set up a condenser in the vertical reflux position and reflux vigorously while stirring the mixture with the magnetic stirrer for an hour.

b) *Isolation of the crude chalcone*

After refluxing, cool the contents of the Erlenmeyer flask in an ice bath. The chalcone should crystallize. If crystals do not appear, scratch the inside wall of the flask with a glass rod. Collect the crystals in a Büchner funnel, wash them with a little ice cold ethanol, then air dry and weigh the crystals.

c) *Recrystallization of the chalcone*

Recrystallize this crude chalcone from ethanol, using a 100 cm^3 beaker. Use the heating plate located in the hood (fume chamber). When the crystallization is over (wait long enough and scratch if necessary), collect the crystals in a Büchner funnel, and air dry them.

Give your entire product to the supervisor who will measure its mass and melting-point.

Do not breathe the vapour while recrystallizing and measuring the melting point. It contains irrigating chalcone!!!

Questions:

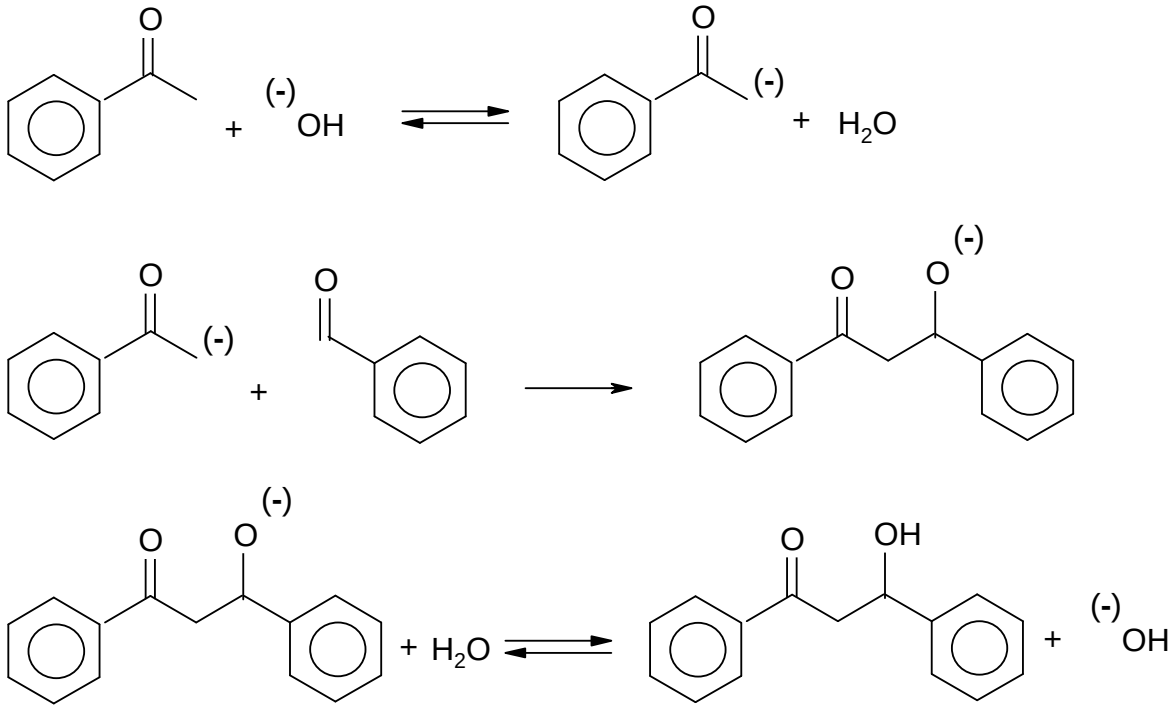
1.1 Write the mechanism for this reaction.

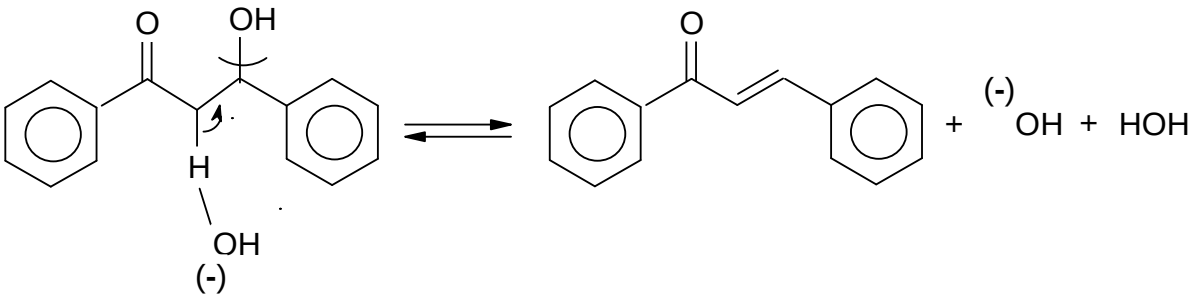
1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.

1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1




O
OH
H
OH
(-)
O
+
(-)
OH + HOH

PROBLEM 2 (Practical)

Qualitative Analysis

Equipment:

Five flasks are labelled 2.1 through 2.5. Each contains an aqueous solution of a colourless metal nitrate. Except for silver nitrate, the concentrations of the nitrates used to prepare these solutions, are all 0.1 mol dm^{-3}.

The solutions are: aluminium(III) nitrate
calcium(II) nitrate
lead(II) nitrate
silver(I) nitrate
zinc(II) nitrate

Moreover, available are pH indicator paper and the following three reagents of a concentration of about 5 mol dm^{-3}, contained in flasks labelled 2.6 through 2.8.

2.6 : hydrochloric acid,

2.7 : aqueous ammonia solution,

2.8 : sodium hydroxide solution.

Beware: these solutions are all concentrated and corrosive.

Tasks:

2.1 Carry out reactions between each reagent and each solution. For each of the solutions 2.1 through 2.5, record your observations for each reaction observed.

2.2 Write the name of the cation contained in each of the solutions 2.1 through 2.5 in the corresponding space on the answer sheet.

2.3 For each cation identified, write the equation for each reaction observed.

SOLUTION

2.1 Aluminium(III) nitrate

- $Al^{3+} + HCl \rightarrow$ no reaction
- $Al^{3+} + 3\ NH_3 + 3\ H_2O \rightarrow Al(OH)_3 \downarrow + 3\ NH_4^+$
- $Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3 \downarrow$

- $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$ (aq)

calcium(II) nitrate

- $Ca^{2+} + HCl \rightarrow$ no reaction
- $Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2 \downarrow$

lead(II) nitrate

- $Pb^{2+} + 2\ Cl^- \rightarrow PbCl_2 \downarrow$ (in cold solutions)
- $Pb^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Pb(OH)_2 \downarrow + 2\ NH_4^+$
- $Pb^{2+} + 2\ OH^- \rightarrow Pb(OH)_2 \downarrow$

  $Pb(OH)_2 + 2\ OH^- \rightarrow [Pb(OH)_4]^{2-}$ (aq)

silver(I) nitrate

- $Ag^+ + Cl^- \rightarrow AgCl \downarrow$
- $Ag^+ + NH_3 + H_2O \rightarrow AgOH \downarrow + NH_4^+$ (or Ag_2O)

  $AgOH + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^+$ (aq) + OH^-
- $Ag^+ + OH^- \rightarrow AgOH \downarrow$

  $2\ AgOH \rightarrow Ag_2O + H_2O$

zinc(II) nitrate

- $Zn^{2+} + HCl \rightarrow$ no reaction
- $Zn^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Zn(OH)_2 \downarrow + 2\ NH_4^+$

  $Zn(OH)_2 + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$(aq) + $2\ OH^-$
- $Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \downarrow$

  $Zn(OH)_2 + 2\ OH^- \rightarrow [Zn(OH)_4]^-$ (aq)

PROBLEM 3 (Practical)

Titration of Oxygen Dissolved in Water

(Winkler's method)

In aqueous alkaline solution, dissolved oxygen oxidizes manganese(II) hydroxide to hydrated manganese(III) oxide (written as $Mn(OH)_3$ for simplification). In acidic solution, manganese(III) ions oxidize iodide ions to iodine. The iodine formed is titrated with a sodium thiosulphate solution.

Data:

Redox couple	Electrode potentials (in V)	
	at *pH* = 0	at *pH* = 14
Mn^{3+} / Mn^{2+}	1.51	
$Mn(OH)_3 / Mn(OH)_2$		0.13
O_2 / H_2O	1.23	0.39
I_2 / I^-	0.62	0.62
$S_4O_6^{2-} / S_2O_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(Mn(OH)_2) = 1\times10^{-13}$

$K_{sp}(Mn(OH)_3) = 1\times10^{-36}$

Gas constant: $R = 8.315$ J $K^{-1}mol^{-1}$

Procedure:

Preliminary remarks: To reduce volume variations, the reagents are added either as solids (sodium hydroxide pellets ...), or as concentrated solutions (sulphuric acid).

1. The water to be tested is stored in a large container located on the general-use bench. Place two glass beads into a 250 cm^3 ground top Erlenmeyer (conical) flask. Fill it to the rim with the water to be tested. At this stage of the manipulation the

Erlenmeyer flask should be standing in the basin provided to avoid overflow of water onto the bench. Measure the temperature of the water.

2. Add to the water, avoiding any loss of reagent:
   a) 2 g of manganese(II) chloride, preweighed within a decigram and contained in the bag.
   b) about 8 pellets of sodium hydroxide (yielding a basic medium, *pH* = 14). The pellets will be found on the general-use bench.
3. Stopper the Erlenmeyer flask, avoiding air bubbles, and swirl it until complete dissolution of the sodium hydroxide and of the manganese chloride has occurred. A brown precipitate forms.
4. Let the flask stand for at least 30 minutes.
5. Open the Erlenmeyer flask, add concentrated sulphuric acid dropwise, stirring with a glass rod until the solution is definitely acidic (check with the *pH* indicator paper); make sure that nearly all the precipitate has disappeared.
   Sulphuric acid will be found on the general-use bench.
6. Add to the Erlenmeyer flask 3 g of potassium iodide, preweighed within a decigram and contained in a bag. Stopper the flask and shake it until the potassium iodide has dissolved. The solution should now be clear.
7. Remove a 50 cm^3 sample of the solution and titrate it with a X mol dm^{-3} sodium thiosulphate solution (the numerical value of X will be shown on the board). For this titration, the endpoint can be determined using the indicator thiodene which is equivalent to starch. A small quantity of this solid indicator should be dissolved in the solution being titrated just prior to the endpoint.

Questions:

3.1 Justify that the oxidation of manganese(II) by dissolved oxygen is possible only in alkaline solution.

3.2 Write the equation of the reaction between:
- dissolved oxygen and manganese(II) hydroxide (in alkaline solution),
- manganese(III) ions and iodide ions,
- iodine and thiosulphate.

3.3 Record the volume of thiosulphate required to reach the endpoint.

3.4 Derive an expression that relates the dissolved oxygen concentration in water (expressed as mol dm^{-3}) to the volume in cm^3 of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm^3), determined at 0 ^oC and at a pressure of 101,325 Pa, contained in a litre of water (measured at ambient temperature). Give the temperature of the water.

_____

SOLUTION

3.1 $E^0(O_2/H_2O) > E^0(Mn(III)/Mn(II)$ at $pH = 14$

3.2 $O_2 + 4\ e^- + 2\ H_2O \rightarrow 4\ OH^-$

$Mn(OH)_2 + HO^- \rightarrow Mn(OH)_3 + e^-$

$O_2 + 4\ Mn(OH)_2 + 2\ H_2O \rightarrow 4\ Mn(OH)_3$

$2\ I^- \rightarrow I_2 + 2\ e^-$

$Mn^{3+} + e^- \rightarrow Mn^{2+}$

$2\ I^- + 2\ Mn^{3+} \rightarrow I_2 + 2\ Mn^{2+}$

$I_2 + 2\ e^- \rightarrow 2\ I^-$

$2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ e^-$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

3.4 1 mol $O_2 \mathrel{\hat{=}}$ 4 mol Mn(II) $\mathrel{\hat{=}}$ 4 mol Mn(III)

4 mol Mn(III) $\mathrel{\hat{=}}$ 4 mol I^- $\mathrel{\hat{=}}$ 2 mol I_2

2 mol $I_2 \mathrel{\hat{=}}$ 4 mol $S_2O_3^{2-}$

$c(S_2O_3^{2-}) \times V(S_2O_3^{2-}) = 4 \times c(O2) \times 50$

PROBLEM 4 (Practical)

Kinetics of an S_N1 Reaction

In an aqueous ethanolic solution, *tert*-butyl chloride (2-chloro-2-methylpropane) undergoes an S_N1 nucleophilic substitution reaction leading to the formation of 2-methylpropan-2-ol and hydrochloric acid:

tert-BuCl + H_2O = *tert*-BuOH + HCl

The rate of the reaction is given by

$$\frac{d[\text{HCl}]}{dt} = k_1 [\textit{tert}\ \text{BuCl}]$$

The aim of this experiment is to determine the rate constant k_1 at ambient temperature.

Procedure:

1. Using a pipette transfer 2.0 cm^3 of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm^3 ground neck Erlenmeyer (conical) flask.
2. As soon as possible add 148 cm^3 (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).
3. Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.
4. After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm^3 samples using a pipette into 20 cm^3 of a mixture of ice and acetone (propanone).

   Add 2 drops of bromothymol blue and titrate the liberated acid with a solution of Y mol dm^{-3} aqueous sodium hydroxide (Y will be shown on the board).

Questions:

4.1 The concentrations of *tert*-BuCl at time $t = 0$ and at time t are linked by the following relationship:

$$\ln \frac{[\text{tertBuCl}]_0}{[\text{tertBuCl}]_t} = k_1.t$$

Establish the theoretical expression:

$$\ln \frac{V_\infty}{V_\infty - V} = k_1\, t$$

where V stands for the volume of sodium hydroxide used at time t and $V(8)$ for the corresponding value at $t(8)$.

$t_\infty = t(8); \quad V_\infty = V(8)$

4.2 Calculate $V(8)$ (density of *tert*-BuCl at 20 ^oC: 850 kg m^{-3}, molar mass of *tert*-BuCl: 92.5 g mol^{-1}).

4.3 Fill in the table on the answer sheet whose columns will be:

t(min), $V(cm^3)$, V_∞, V, $\frac{V_\infty}{V_\infty - V}$, $\ln \frac{V_\infty}{V_\infty - V}$

Draw the curve

$$\ln \frac{V_\infty}{V_\infty - V} = f(t)$$

4.4 Determine the value of k_1 (give the value of $t(0)$).

SOLUTION

4.1

	t-BuCl + H_2O $\rightarrow$ t-BuOH + HCl	
$t = 0$	$(t\text{-BuCl})_0$	
t	(t-BuCl)	$(t\text{-BuCl})_0 - (t\text{-BuCl})$
$t(8)$		$(t\text{-BuCl})_0$

$$\frac{d(\text{HCl})}{dt} = -\frac{(t - \text{BuCl})}{dt} = k_1 (t - \text{BuCl})$$

$$\ln \frac{(t - BuCl)_0}{(t - BuCl)} = k_1 t$$

t:

$$c(\text{HCl}) = c_0(\text{t-BuCl}) - c(\text{t-BuCl}) = \frac{V(\text{NaOH}) \times c(\text{NaOH})}{V(\text{HCl})} = \frac{V \times \text{Y} \times 10^{-2}}{10}$$

$t(8)$

$$c(\text{HCl}) = c_0(\text{t-BuCl}) = \frac{a\,Y}{10}$$

$$c(\text{t-BuCl}) = \frac{(a - V)\,\text{Y}}{10}$$

$$\ln\frac{c_0(\text{t-BuCl})}{c(\text{t-BuCl})} = \ln\frac{a}{a-V} = k_1\, t$$

4.2 $n_0(\text{t-BuCl}) = \dfrac{1.70}{92.5}$ $\qquad M(\text{t-BuCl}) = 92.5 \text{ g mol}^{-1}$

$$Y \times a \times 10^{-3} = \frac{10}{150} \times n_0(\text{t-BuCl})$$

$$a_{(\text{ml})} = \frac{170}{Y \times 10^{-3} \times 15 \times 92.5}$$