Lab: Hydrolysis of Organic Halogen Compounds

Introduction

In this experiment, you will compare the rates of hydrolysis of 1-chlorobutane, 1-bromobutane, 1-iodobutane and chlorobenzene. A general equation for the hydrolysis is :

$$R\text{-}X + H_2O \longrightarrow R\text{-}OH + H^{+1} + X^{-1}$$

(where R = alkyl or aryl group; X = halogen atom).

The rate of the reaction may be followed by carrying it out in the presence of silver ions, so that any halide ions produced form a silver halide precipitate:

$$Ag^{+1}_{(aq)} + X^{-1}_{(aq)} \longrightarrow AgX_{(s)}$$

Note: AgCl: white ppte., AgBr: cream ppte., AgI: yellow ppte.

Since halogenalkanes and halogenarenes are insoluble in water, ethanol is added to act as a common solvent for the halogeno-compounds and silver ions.

Purpose

To determine how the rate of hydrolysis of an organic halogen compound depends on:

a) the identity of the halogen atom,

b) the nature of the carbon-hydrogen 'skeleton'

Requirements

5 tt fitted with cork, tt rack, water bath set at 60 ^{0}C, waterproof pen,10 cm^3 measuring cylinder, thermometer, stop-clock (or clock with seconds hand), ethanol, C_2H_5OH, 1-chlorobutane,C_4H_9Cl 1-bromobutane, C_4H_9Br, 1-iodobutane, C_4H_9I, chlorobenzene, C_6H_5Cl, 0.05 mol dm^{-3} $AgNO_{3(aq)}$

Safety

All organic halogen compounds have harmful vapours and can be toxic by absorption through the skin. Some are flammable. Therefore you must:

a) keep the stoppers on the bottles as much as possible, (b) keep the bottles away from the flames.

As only small quantities are being used there are no particular hazards associated with this lab. however it is worth noting that some chlorinated organic compounds e.g. dioxin, 2,4,5-trichlorophenoxyethanoic acid (Agent Orange) and polychlorinated biphenyls (PCB,s) can be extremely poisonous.

Procedure

1. Set up the water bath using an electric hot plate , set at a temperature of 60 ^{0}C.
2. Make sure none of the tts contains any tap-water; this would give an immediate precipitate with $AgNO_{3(aq)}$ and skew your results. Use dry tts.
3. Pour 2 cm^3 of ethanol into each of the four tts and mark them with the letters A to D.
4. Add 3-4 drops of 1-chlorobutane, C_4H_9Cl to A, 3-4 drops of 1-bromobutane, C_4H_9Br to B, 3-4 drops of 1-iodobutane, C_4H_9I to C and 3-4 drops of chlorobenzene to D.
5. Pour ~ 5 cm^3 of silver nitrate solution into the fifth tt.
6. Stand all the tts in the beaker (or water-bath) and heat to 60 ^{0}C, then stop heating
7. Quickly add 1 cm^3 of aqueous silver nitrate to each of the tts A to D and start the stop-clock. Shake each tt once to mix the contents, and leave in the water with the cork resting **loosly** on the tt to stop evaporation.
8. Watch the tts continuously for about 10 mins. and note in the Data Table, the time when a precipitate first appears in each tt as a definite cloudiness. If necessary, heat the water to 60 ^{0}C again at intervals.
9. Continue observations for ~ 30 mins. more, noting any further changes in the appearance of the precipitates.

Data Table

Reaction	Time for precipitate to appear	Observations
A 1-chlorobutane, C_4H_9Cl		
B 1-bromobutane, C_4H_9Br		
C 1-iodobutane, C_4H_9I		
D Chlorobenzene		

Questions

1. What types of reagents (electrophiles or nucleophiles) react with halogenoalkanes? Explain your answer in terms of the polarity of the carbon-halogen bond.

2. List the compounds in order of speed of hydrolysis, fastest first.

3. Compare the strengths of the carbon-halogen bonds, and state if the bond strengths agree with your observations.
   C - Cl: 338 kJ mol^{-1}, C - Br: 276 kJ mol^{-1}, C - I: 238 kJ mol^{-1},
   C - Cl in chlorobenzene: 365 kJ mol^{-1}

4. Write equations for the hydrolysis reactions which take place in this experiment.

5 Does changing the halogen atom have an effect on the rate of hydrolysis? If so, explain why.

6. Explain the reactivity or the lack of reactivity observed for the hydrolysis of chlorobenzene.

Conclusion

Extension

1. Suggest a reason why iodoalkanes are often used in organic chemistry in preference to the corresponding bromine or chlorine compounds.

2. 'Non-stick' frying pans are coated with an organic fluoro-compound, PTFE (polytetrafluoroethene). Why is there little risk of food contanination by the fluorine?

3. What are (a) the products of hydrolysis, (b) what is the expected mechanism of hydrolysis, and (c) what is the intermediate of the hydrolysis for each of the following ...

   i) $CH_3CH_2CH_2CH_2Cl$

   ii) $CH_3CH_2CHClCH_3$

   iii) $(CH_3)_3Cl$

   iv) meta-bromo toluene

4. Explain why nucleophilic attack is difficult for chlorobenzene.

5. For each of the following pairs of compounds, give one simple chemical test that would distinguish between them. For each compound, describe exactly what you would observe (if anything) and explain the reactions which have occurred.

   a) $CH_3CH_2CH_2I$ and $CH_3CH_2CH_2Cl$

   b) (chloromethyl)benzene and 4-chlorotoluene

6. Explain how you would synthesis:
   a) $CH_3CH_2CH_2Br$ ---------> $CH_3CHBrCH_2Br$

   b) Toluene ----------> $C_6H_5CH_2CN$