

Name: Chow Ching Yue (7) Group: 4 Grade: _____
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Preparation of a Halogen Compounds

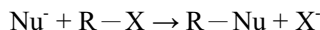
Aim

The purpose of this experiment is to find how the rate of hydrolysis of an organic halogen compound depends on:

- the identity of the halogen atom,
- the nature of the carbon-hydrogen 'skeleton'.

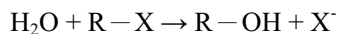
Theory

Halogen-compounds are organic compounds composed of carbon, hydrogen and halogen. One of the characteristic reactions of halogenoalkanes is nucleophilic substitution reactions. A general equation for the nucleophilic substitution is:

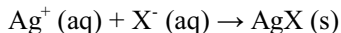


(where R = alkyl group, X = halogen atom)

In this experiment, the rates of hydrolysis of 1-chlorobutane, 1-bromobutane, 1-iodobutane and chlorobenzene are compared. The nucleophile in this substitution is H_2O . OH^- attacks the carbocation and displaces a halide ion from the halogenalkane, which is called hydrolysis. A general equation for the hydrolysis is:



As the halide ions substituted can be identified by silver nitrate solution,



the rate of reaction can be followed by time for the first appearance of precipitate.

Since halogenoalkanes and halogenoarenes are insoluble in water while silver ions dissolve in aqueous solution, ethanol is added to the solution to act as a common solvent for halogeno-compounds and silver ions.

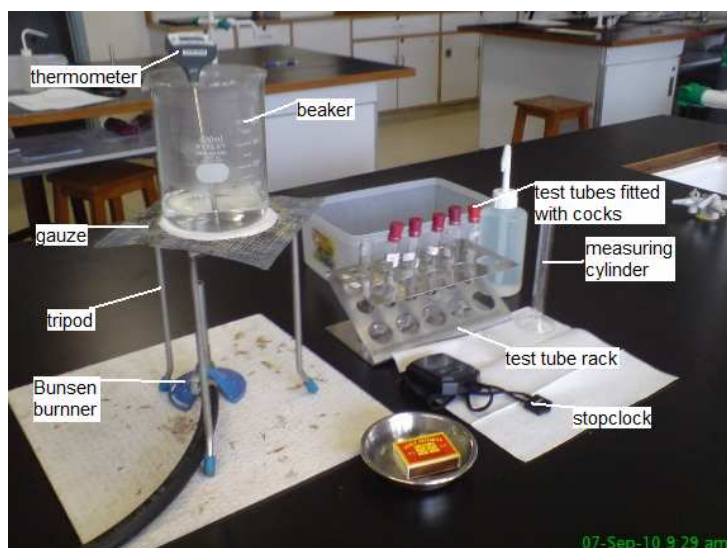
In this experiment, the variables are:

Controlled variables	Independent variable	Dependent variable
<ul style="list-style-type: none"> ● Temperature ● Concentration and Volume of silver nitrate solution used ● Drops of Haloalkane/Halobenzene added, ● Volume of Ethanol used 	<ul style="list-style-type: none"> ● Species of Halogen compound used 	<ul style="list-style-type: none"> ● Time for the first appearance of precipitate










Requirements

Apparatus				
Safety spectacles	× 1		Bunsen burner	× 1
Tripod	× 1		Gauze	× 1
Bench protection sheet	× 1		Beaker, 250cm ³	× 1
Thermometer	× 1		Test-tubes with corks	× 5
Test tube rack	× 1		Protective plastic gloves	× 1
Measuring cylinder	× 1		Stopclock	× 1

Chemicals				
ethanol, C ₂ H ₅ OH			1-chlorobutane, C ₄ H ₉ Cl	
1-bromobutane, C ₄ H ₉ Br			1-iodobutane, C ₄ H ₉ I	
chlorobenzene, C ₆ H ₅ Cl			silver nitrate solution, AgNO ₃	0.05M



Hazard warnings

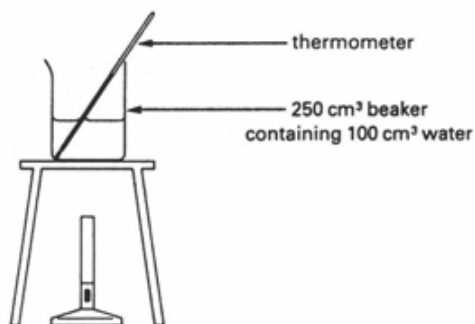
1-chlorobutane		1-bromobutane	
1-iodobutane	 	chlorobenzene	
Ethanol	 	silver nitrate	 

As all organic compounds have harmful vapors and can be toxic by absorption through the skin. Some are flammable. We must:

1. keep the stoppers in the bottles as much as possible
2. keep the bottles away from flames
3. wear safety spectacles and gloves
4. carry out experiment in good ventilation

Procedure

1. Apparatus were set up as shown in Fig. 1. All test tubes were made sure not containing any tap-water.



2. 2cm³ of ethanol was poured into each of four test-tubes and they were marked with letters A to D

3. 3-4 drops of 1-chlorobutane was added to A, 3-4 drops of 1-bromobutane was added to B, 3-4 drops of 1-iodobutane to C and 3-4 drops chlorobenzene was added to D.
4. 5cm³ of silver nitrate solution was poured into the fifth test-tube.



5. All the test-tubes were placed in the beaker and heated to 60°C. Then, the Bunsen burner was removed.



6. 1cm³ of aqueous silver nitrate was quickly added to each of the tubes A to D and the stopclock was started. Each tube was shaken once to mix the contents, and was left in the water with the cork resting loosely on the tube to reduce evaporation.

7. The tubes were being watched continuously for about ten minutes and the time when a precipitate first appears in each tube as a definite cloudiness was noted. The water was heated to 60 again at intervals.
8. Tubes were being observed at intervals for about 30 minutes more, noted for any further changes in the appearance of the precipitates.

Results Table

Triad 1

Test 2

Melting Point of 2,4-dinitrophenylhydrazones/°C 123-128 127-128

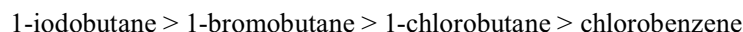
Structural formula of the Unknown carbonyl compound

Chemical name of the unknown carbonyl compound propanone

Reaction	Time for the first appearance of precipitate / s	Observations
A. 1-chlorobutane	3	white precipitate is formed
B. 1-bromobutane	13	yellow precipitate is formed
C. 1-iodobutane	700	small amount of white precipitate is formed
D. chlorobenzene	/	no observation

Interpretation of results

From the experimental results, compounds in order of speed of hydrolysis, from fastest rate first are:

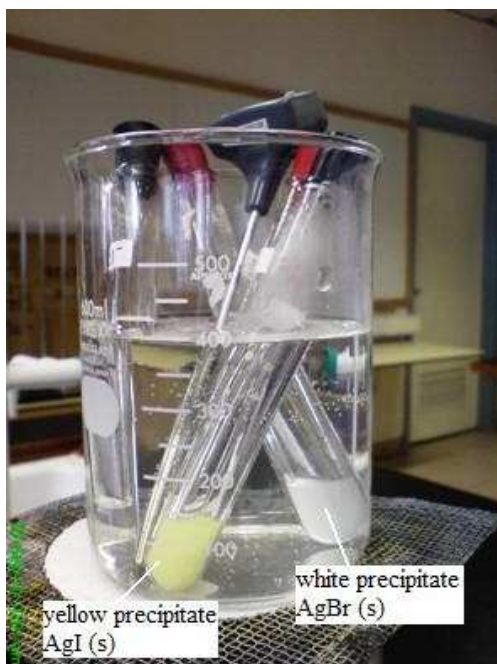


We can compare the rate of hydrolysis of halogen-compounds in 2 categories. The first one is among the haloalkanes (1-chlorobutane, 1-bromobutane and 1-iodobutane), and the second one is between haloalkane and halobenzene.

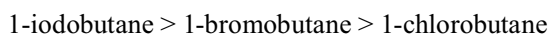
1. Among the haloalkanes (1-chlorobutane, 1-bromobutane and 1-iodobutane)

All three haloalkanes give positive result, i.e. precipitate formed, in the experiment.

The equations are:



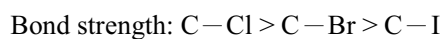
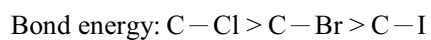
The rates of hydrolysis among 3 haloalkanes, fastest rate first are:



Consider the bond energy of haloalkanes:

Bond (in haloalkanes)	Bond energy / kJ mol^{-1}
C—Cl	338
C—Br	276
C—I	238

Since the rate determining step involves the bond breaking of the between the C—X bond in the haloalkane, where X = Cl, Br or I. The greater the bond energy, the greater the bond strength and the lower the reactivity, therefore:

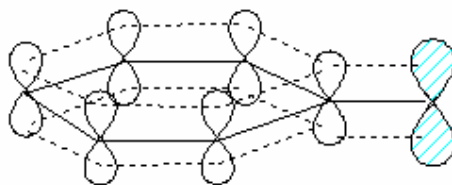


As least energy is required to break the C—I bond, it is the weakest bond and most reactive, therefore the rate of hydrolysis of 1-iodobutane is the greatest, vice versa.

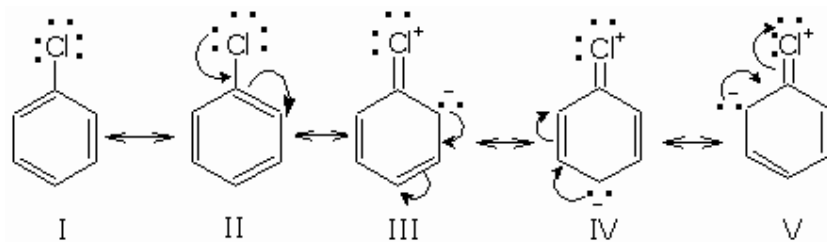
2. Between haloalkane and halobenzene

All the haloalkanes give positive result but the halobenzene (chlorobenzene) give a negative result, i.e. no observable change in the experiment.

The reactivity of halobenzene is much lower than that of haloalkanes. In chlorobenzene, the lone-pair electrons of chlorine become involved in the π -electron system of the benzene ring.



The p-orbital of the Cl atom interact with those of the ring, causing a drift of electrons towards the degree of polarity of C—Cl bond, the C—Cl bond has partial double bond nature. This also account for the high C—Cl bond energy in chlorobenzene, 365 kJ mol⁻¹, compare with those of halogalkanes.



Therefore, chlorobenzene (halobenzenes) is comparatively inert and only undergo nucleophilic substitution of the Cl atom with extreme difficulty.

Discussion on Errors

1. There was time lag on adding AgNO₃ solution into different halogen compounds. For example, the stopclock was started when adding the AgNO₃ solution into the first test tube. Time lag existed when adding AgNO₃ solution into following tubes. Thus, time measured for the first appearance of precipitate is longer than the actual one.

We can use separate stopclock for each set of data, i.e. one stopclock is responsible for measuring the time for first appearance of precipitate of one chemical only. Thus, the time lag in measuring can be reduced. Or we can have more technicians involved in the experiment to pour the AgNO_3 solution into the test tubes at the same time.

2. There were impurities left of the test tubes. Once the AgNO_3 solution was added, the solution gave precipitate immediately. The time measured was not because of the release of halogen during the substitution.

We can make sure the test tubes do not contain any water. Clear test tubes should be used.

3. All the halogeno-compounds used in the experiment are volatile. The chemicals may evaporate during the experiment, leading to loss of chemicals.

Cover the tubes with stoppers loosely to minimize the effect of evaporation of chemicals.

4. The temperature of the water bath was not constant, which affected the rate of reaction. Thus, the time for first appearance of precipitate was affected.

Use an electrical water bath to keep the temperature of the chemicals constant.

Conclusion

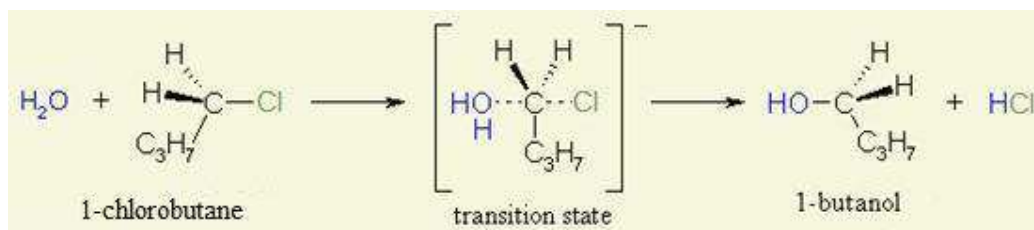
The rate of hydrolysis of 1-iodobutane is the fastest, followed by 1-bromobutane, 1-chlorobutane and chlorobenzene. The rate of hydrolysis of haloalkane is greater than that of halobenzene, while it increases with the decrease bond strength between the carbon atom and the leaving group.

Questions and Answers

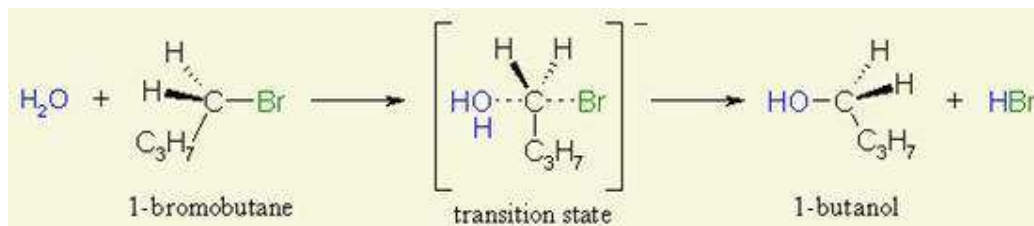
1. chlorobenzene < 1-chlorobutane < 1-bromobutane < 1-iodobutane

2. 1-iodobutane > 1-bromobutane > 1-chlorobutane > chlorobenzene

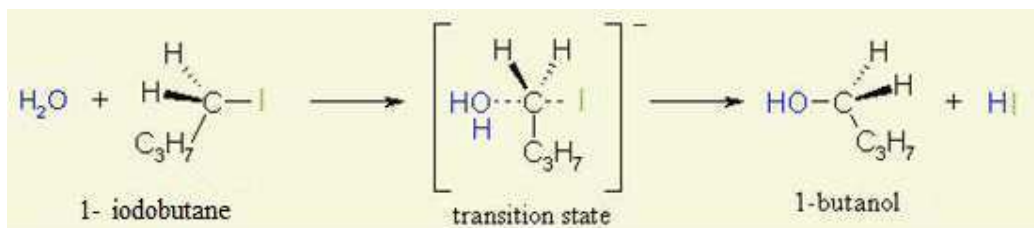
3. 1-chlorobutane:



1-bromobutane:



1-iodobutane:



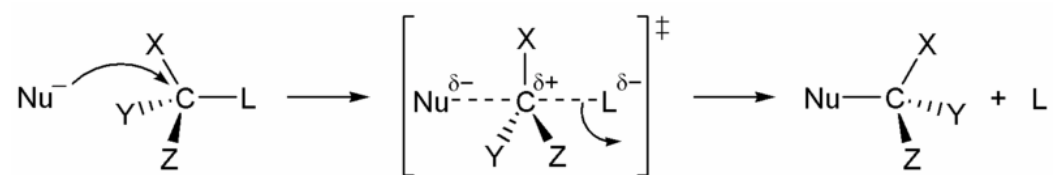
Comment

1. S_N2 mechanism

The hydrolysis of organic halogen compounds is a kind of nucleophilic substitution. As all the halogen compounds used in this experiment are primary halogen compounds, the primary carbocation is unstable and the steric hindrance is small, which favored the S_N2 mechanism.

Therefore, halogen compounds in this experiment undergo S_N2 mechanism more readily,

here is the general equation for the S_N2 mechanism is:



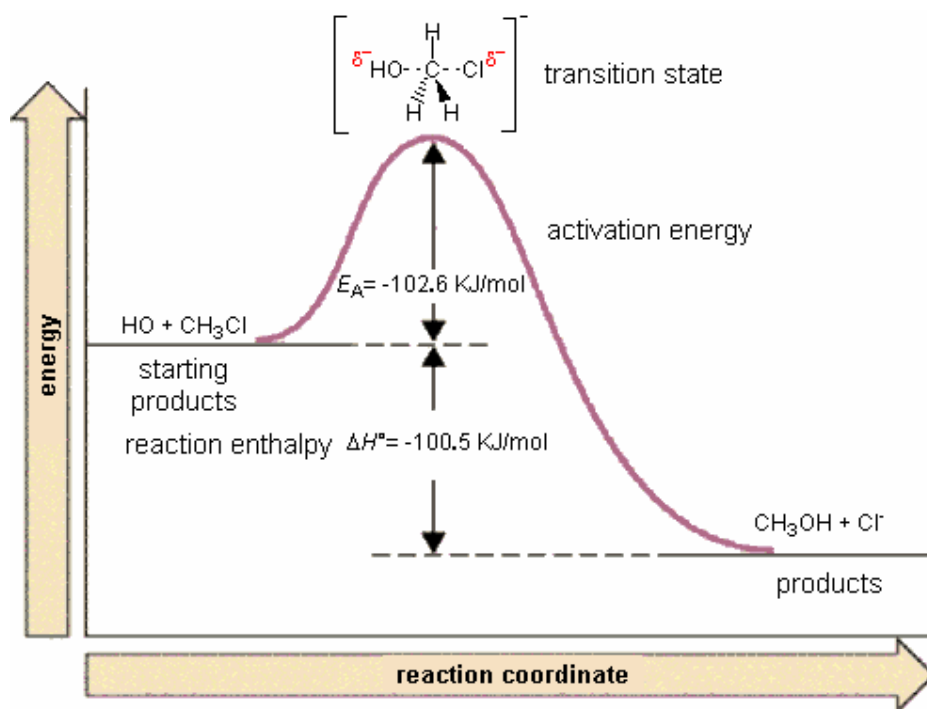
The term S_N2 stands for Substitution reaction, Nucleophilic, 2nd order. According to the S_N2 mechanism, there is a single transition state because bond-breaking and bond-making occur simultaneously, which is a one-step reaction mechanism. For this to occur, the nucleophile approach from the backside of the carbon-leaving group bond (so-called backside attack). There is not intermediate in an S_N2 reaction, just a transition state. A transition state has no real lifetime, it is the highest energy point on the reaction coordinate as starting materials transition into products.

In this reaction, a new bond is formed between the nucleophile, H₂O, and the carbon atom, while the carbon-halogen bond is broken. The departing halogen is referred to as the leaving group. The species being attacked by the nucleophile is referred to as the electrophile.

S_N2 is a second order kinetics, rate of reaction is totally depended on both [OH⁻] and [RX]

$$\text{Rate} = k [\text{RX}] [\text{OH}^-]$$

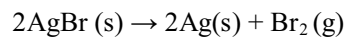
The energy level diagram of the S_N2 reaction:



2. Photodecomposition of AgBr(s)

At the end of the experiment, it was found that the solution containing AgBr(s) turns from pale yellow to grey. This is due to the decomposition of AgBr(s) in the presence of sunlight.





3. Nucleophilic substitution of halobenzenes

As the lone-pair electrons of the halogen become involved in the π -electron system in the aromatic ring, the halobenzenes are comparatively inert and only undergo nucleophilic substitution with extreme difficulty

Under 300 °C, 200 atm, halobenzenes undergo nucleophilic substitution with presence of conc. NaOH to give phenol, C₆H₅OH.

Reference

1. Study Guide Chapter 30
P. 7, 12-13
2. Haloalkanes
<http://chemophile.pbworks.com/f/Halogenoalkanes.pdf>
3. AUS-e-TUTE
<http://www.usetute.com.au/index.html>