Chem Factsheet

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Factors Affecting the Rate of Hydrolysis of Haloalkanes

To succeed in this topic you need to:
- be able to draw the structures of primary, secondary and tertiary haloalkanes
- be able to explain the nucleophilic substitution of a haloalkane with water or hydroxide ions to make an alcohol
- know how to test for halide ions using silver nitrate
- explain the factors which affect the rates of all reactions

After working through this Factsheet you will:
- understand how to measure the rate of hydrolysis of haloalkanes
- be able to explain the factors that affect the rate of hydrolysis of haloalkanes
- understand how changing the conditions can promote elimination rather than substitution

What is the hydrolysis of haloalkanes?

Hydrolysis means a reaction with water where the water molecule is split. Hydrolysis of a haloalkane (R-X) produces an alcohol (R-OH) as shown in Equation 1.

Equation 1 $R{-}X + H_2O \longrightarrow R{-}OH + HX$

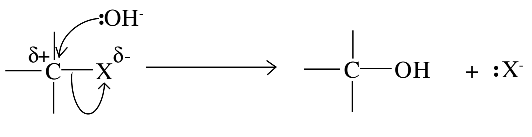
The reaction can take place by the action of water or hydroxide ions. It is very slow with water, even when heated, and so hydroxide ions, OH^-, (from a solution of sodium or potassium hydroxide) are commonly used as shown in Equation 2.

Equation 2 $R{-}X + OH^- \xrightarrow[\text{heat}]{\text{NaOH (aq)}} R{-}OH + X^-$

The mechanism of the reaction is a nucleophilic substitution. Depending on whether the haloalkane is primary, secondary or tertiary, the reaction can take place in a single step (S_N2 – second order nucleophilic substitution) or two steps (S_N1 – first order nucleophilic substitution).

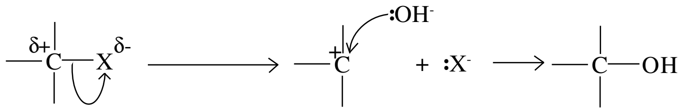
In the S_N2 case (Fig 1), the reaction is initiated by attack of the nucleophile (OH^-) on the δ+ carbon atom attached to the electronegative halogen. The oxygen atom donates a lone pair of electrons to form a bond with the carbon atom, causing the carbon-halogen bond to break.

Fig 1. S_N2 mechanism of the nucleophilic substitution of a haloalkane with a hydroxide ion



In the S_N1 case (Fig 2.), the reaction is initiated by the breaking of the carbon-halogen bond to form a carbocation. The nucleophile (OH^-) then bonds to the C+ atom by donating a lone pair of electrons from the oxygen atom to form a bond.

Fig 2: S_N1 mechanism of the nucleophilic substitution of a haloalkane with a hydroxide ion



***Exam Hint:** Be careful when you draw curly arrows in mechanisms. Each arrow signifies the movement of a pair of electrons. Make sure that the arrow starts from the lone pair of electrons on the oxygen, and points to the carbon atom. The second arrow starts from the bond between the carbon and the halogen, and ends on the halogen.*

Note: Currently, only one A level specification includes the details of the S_N1 mechanism. If you need to know more about the S_N1 mechanism, see FactSheet 40, Reaction Mechanisms.

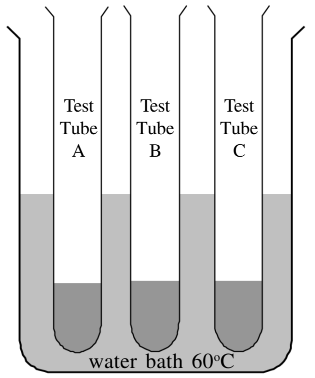
How can you measure the rate of hydrolysis of haloalkanes?

Equations 1 and 2 show that hydrolysis of a haloalkane releases halide ions into the reaction mixture. The formation of the halide ions (except fluoride, F^-, ions) can be detected by the addition of silver nitrate solution, which reacts to make a silver halide precipitate (Equation 3). This does not apply to fluoro compounds because silver fluoride is soluble in water.

Equation 3 $X^-(aq) + Ag^+(aq) \rightarrow AgX(s)$

This simple reaction provides a means of following the progress of the reaction, since the time taken to produce the silver halide precipitate can be measured, and this gives a measure of the rate of substitution of halide ions from the haloalkane. Fig 3 shows a typical experiment.

Fig 3. Measuring the rate of hydrolysis of haloalkanes using silver halide precipitates



In this experiment, water is used as the nucleophile rather than hydroxide ions to give a reasonably slow rate of reaction which is easier to measure. Also, haloalkanes are only sparingly soluble in water, so ethanol is added to the tubes as a solvent to ensure that both the silver nitrate solution and the halobutane are miscible.

	Contents of test tube	Time taken for precipitate to form (/s)
A	0.5 cm^3 1-chlorobutane + 3 cm^3 ethanol + 1 cm^3 dilute $AgNO_3$ (aq)	115
B	0.5 cm^3 1-bromobutane + 3 cm^3 ethanol + 1 cm^3 dilute $AgNO_3$ (aq)	31
C	0.5 cm^3 1-iodobutane + 3 cm^3 ethanol + 1 cm^3 dilute $AgNO_3$ (aq)	3

What affects the rate of the hydrolysis?

Four factors can affect the rate of the hydrolysis reaction: temperature, concentration, the halogen atom and the structure of the haloalkane. We will also look at one factor which does *not* affect the rate of the reaction: the polarity of the carbon-halogen bond.

Temperature and concentration

As you would expect, the rate of hydrolysis can be affected by temperature and concentration. Increasing the temperature will increase the rate of the reaction by increasing the fraction of particles with energy greater than or equal to the activation energy. Increasing the concentration of the solutions will increase the number of collisions between particles and thereby increase the rate. For more on this, see FactSheet 10, Kinetics I – Rates of Reaction.

The halogen atom

The halogen has an important part to play in determining the rate of this reaction. The results of the experiment described above show the silver halide precipitate forms in the following order of rate: iodobutane > bromobutane > chlorobutane.

The rate of hydrolysis is linked to the C-X bond enthalpy (which is equivalent to the bond strength) of the carbon-halogen bond (Table 1).

Table 1: The link between rate of hydrolysis and carbon-halogen bond enthalpy

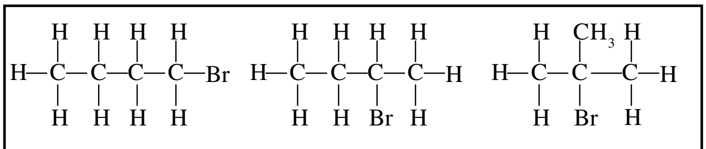
	Relative rate of hydrolysis	Average bond enthalpy (/kJmol^{-1})
C-F	Very slow	+484
C-Cl	Slow	+338
C-Br	Reasonable	+276
C-I	Fast	+238

The carbon-iodine bond has the lowest bond enthalpy. This means that it requires the least energy to break and is therefore hydrolysed *most* rapidly. Conversely, carbon-fluorine bonds are the strongest, and are therefore hydrolysed *least* rapidly.

The structure of the haloalkane

The structure of the haloalkane also has an effect on the rate. To investigate this, you could carry out the same experiment described above, but using a primary, secondary and tertiary haloalkane with a fixed C-X bond (Fig 4).

Fig 4. Primary, secondary and tertiary bromoalkanes



1-bromobutane primary

2-bromobutane secondary

2-bromomethylpropane tertiary

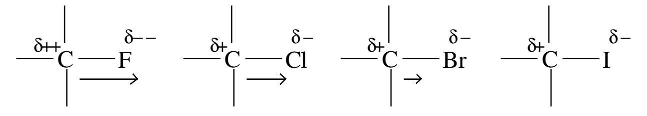
The experiment would show the following order of rate of hydrolysis: tertiary > secondary > primary.

The reason for this is the mechanism of the reaction changes. Tertiary haloalkanes follow an S_N1 mechanism (Fig 2), and described in Factsheet 40, Reaction Mechanisms). This mechanism is faster, all other things being equal, than the S_N2 mechanism (Fig 1), which is typically followed by primary haloalkanes. Secondary haloalkanes react by a mixture of the two mechanisms and so have intermediate rates of hydrolysis.

The polarity of the carbon-halogen bond

It might be expected that the polarity of the carbon-halogen bond would affect the rate of the hydrolysis reaction. Since fluorine is the most electronegative element, the C-F bond is the most polar (Fig 5) and you could predict that the carbon of the carbon-fluorine bond would be more susceptible to attack by nucleophiles than the carbon in the other haloalkanes.

Fig 5. Polarity of the carbon-halogen bonds



Carbon and iodine are so similar in electronegativity (Table 2) that the bond is almost non-polar.

Table 2. Electronegativity values of carbon and the halogens

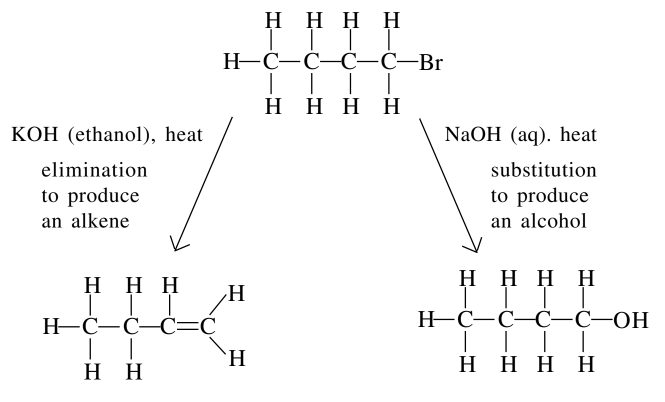
	Electronegativity value
C	2.55
F	3.98
Cl	3.16
Br	2.96
I	2.66

However, experiment clearly shows that the iodoalkane reacts most quickly. This indicates that the reactivity of the haloalkanes is controlled by the strength (or weakness) of the carbon-halogen bond and *not* the polarity of the carbon-halogen bond.

What about elimination?

If potassium hydroxide in a solution of ethanol is used, elimination is favoured over substitution, producing an alkene (Fig 6).

Fig 6. Elimination and substitution of a primary haloalkane



The structure of the haloalkane can have an effect on whether substitution or elimination is favoured, with elimination being more likely with a tertiary haloalkane. However, with any haloalkane, using potassium hydroxide *in ethanol with prolonged heating* is more likely to lead to elimination than substitution. This reaction is described in FactSheet 16, Organic Chemistry II – Reactions I.

Practice Questions

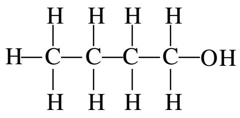
1. Draw and name the products of the reaction of the following haloalkanes with aqueous sodium hydroxide solution:
   (a) 1-bromobutane
   (b) 2-iodobutane
   (c) 2-bromomethylpropane
   (d) 3-bromopentane
   (e) bromocyclohexane

2. Put these haloalkanes in order of increasing rate of hydrolysis, explaining your order: 2-bromobutane, 2-iodobutane, 2-chlorobutane, 2-iodomethylpropane, 1-chlorobutane

3. State and explain the effect of each of the following changes on the rate of hydrolysis of haloalkanes:
   (a) Concentration
   (b) Temperature
   (c) Bond polarity
   (d) Bond enthalpy
   (e) Structure of the haloalkane (primary, secondary or tertiary)

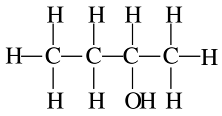
Answers

1. (a)



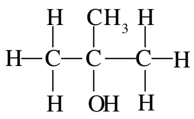
butan-1-ol

(b)



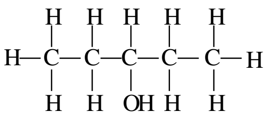
butan-2-ol

(c)



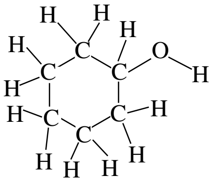
methylpropan-2-ol

(d)



pentan-3-ol

(e)



cyclohexanol

2. Fastest: 2-iodomethylpropane (tertiary) > 2-iodobutane (secondary iodoalkane) > 2-bromobutane (secondary bromoalkane) > 2-chlorobutane (secondary chloroalkane) > 1-chlorobutane (primary chloroalkane)

3. (a) Concentration – Increasing concentration increases the rate of hydrolysis by increasing the number of collisions between particles

   (b) Temperature – Increasing temperature increases the rate of hydrolysis by increasing the fraction of particles with energy greater than or equal to the activation energy

   (c) Bond polarity – Bond polarity has no discernable effect on the rate of the reaction

   (d) Bond enthalpy – The lower the carbon-halogen bond enthalpy, the more reactive the haloalkane. Iodoalkanes have the lowest bond enthalpy and are therefore the most reactive haloalkanes

   (e) Structure of the haloalkane (primary, secondary or tertiary) – Tertiary haloalkanes react more quickly than secondary, which react more quickly than primary. This is due to the mechanism of the reaction.

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