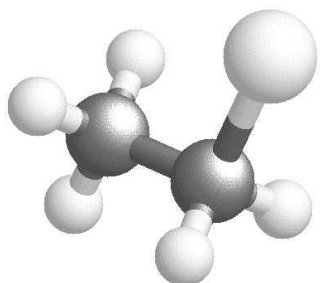




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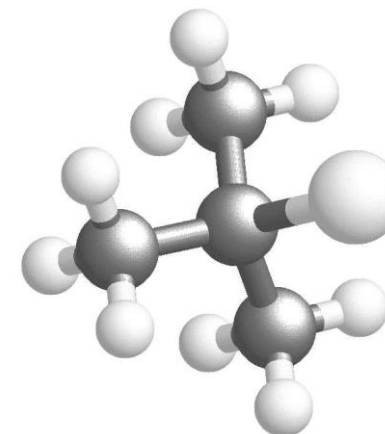


The primary halogenoalkane bromomethane reacts via an S_N2 mechanism.

Chemistry of the Halogenoalkanes

S_N1 and S_N2 Reaction Mechanisms

By Dr. Chris Slatter



The tertiary halogenoalkane 2-bromo-2-methylpropane reacts via an S_N1 mechanism.

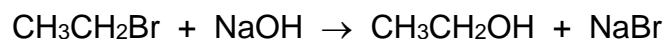
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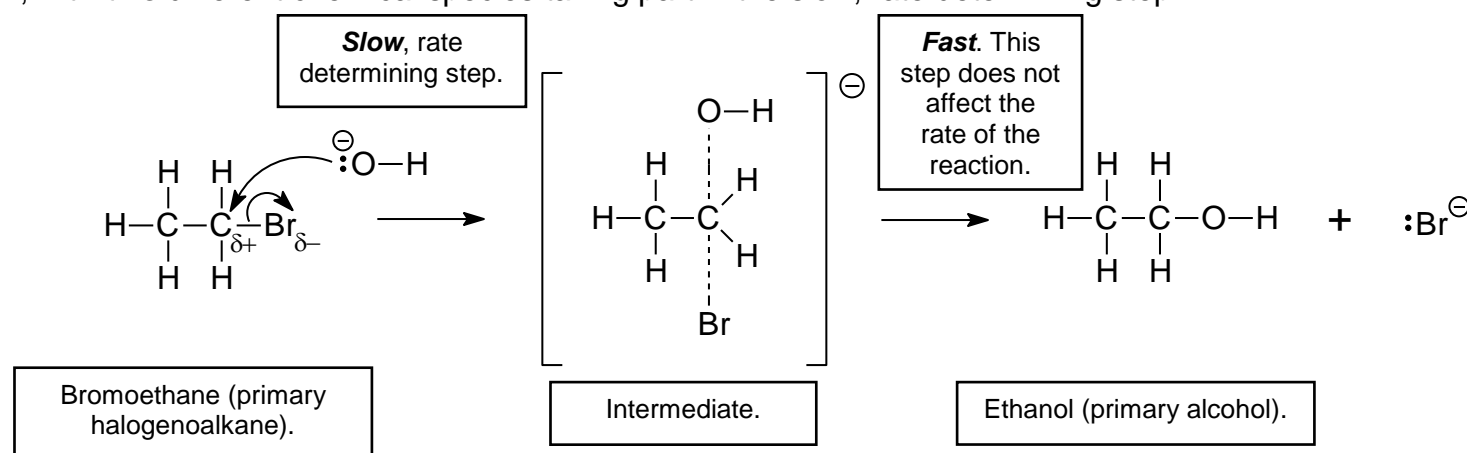
Nucleophilic Substitution into Halogenoalkanes

The S_N2 reaction Mechanism for Primary Halogenoalkanes

An example of a primary halogenoalkane is bromoethane. When bromoethane is refluxed with an aqueous solution of sodium hydroxide, the nucleophilic hydroxide ion substitutes the bromine of the primary halogenoalkane to form the primary alcohol ethanol:



The reaction takes place via an **S_N2** reaction mechanism. This means that the reaction takes place via a **nucleophilic substitution** mechanism, with **two** different chemical species taking part in the slow, rate determining step:



Due to a difference in electronegativity values, the carbon-to-bromine bond of the primary halogenoalkane is polarised $\delta^+ \text{C} - \text{Br} \delta^-$, the more electronegative bromine atom attracting the bonding pair electrons away from the less electronegative carbon atom. Because opposite charges attract, the negative hydroxide ion is attracted towards the δ^+ carbon atom of the primary halogenoalkane. As a covalent bond starts to form between the oxygen of the hydroxide ion and carbon atom of the primary halogenoalkane, the carbon-to-bromine covalent bond of the primary halogenoalkane starts to break.

A negatively charged intermediate is very briefly formed in which both the attacking species and leaving species are both attached to the same carbon atom at the same time.

Nucleophilic attack by the hydroxide ion on the primary halogenoalkane is the slowest stage of the reaction and therefore controls the overall rate of the reaction. Because the primary halogenoalkane and hydroxide ion are **both** involved in the slow, rate determining stage of the reaction, changing the concentration of either one of these two chemicals will directly affect the rate of the reaction.

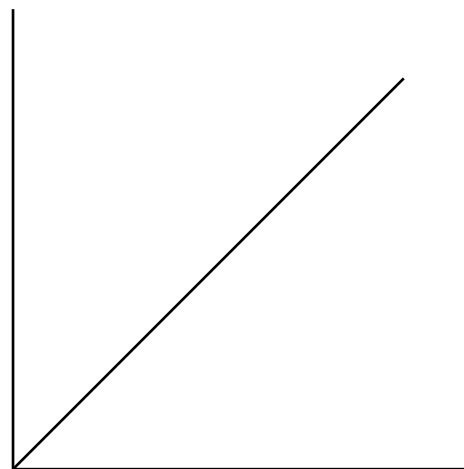
The rate expression for this reaction is written as:

$$\text{Rate} = k \times [\text{primary halogenoalkane}]^1 \times [\text{OH}^-]^1 \text{ (first order with respect to the primary halogenoalkane and first order with respect to the hydroxide ions)}$$

The rate at which the primary halogenoalkane is converted into a primary alcohol is therefore **directly proportional** to the concentration of the primary halogenoalkane and is also **directly proportional** to the concentration of the hydroxide ions (see graphs below):

The rate at which the primary halogenoalkane is converted into a primary alcohol is directly proportional to the concentration of the primary halogenoalkane.

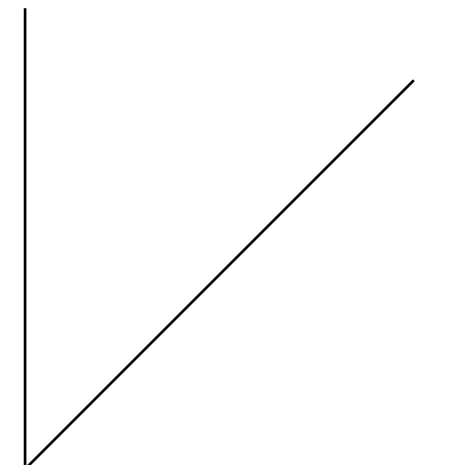
Rate of reaction
/ mol dm⁻³ s⁻¹



Concentration of
primary
halogenoalkane
/ mol dm⁻³

The rate at which the primary halogenoalkane is converted into a primary alcohol is directly proportional to the concentration of the hydroxide ions.

Rate of reaction
/ mol dm⁻³ s⁻¹



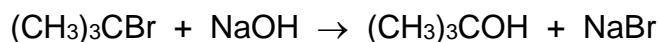
Concentration of
hydroxide ions /
mol dm⁻³

Finally, once the reaction intermediate has formed, it rapidly breaks down to yield the primary alcohol and a bromide ion.

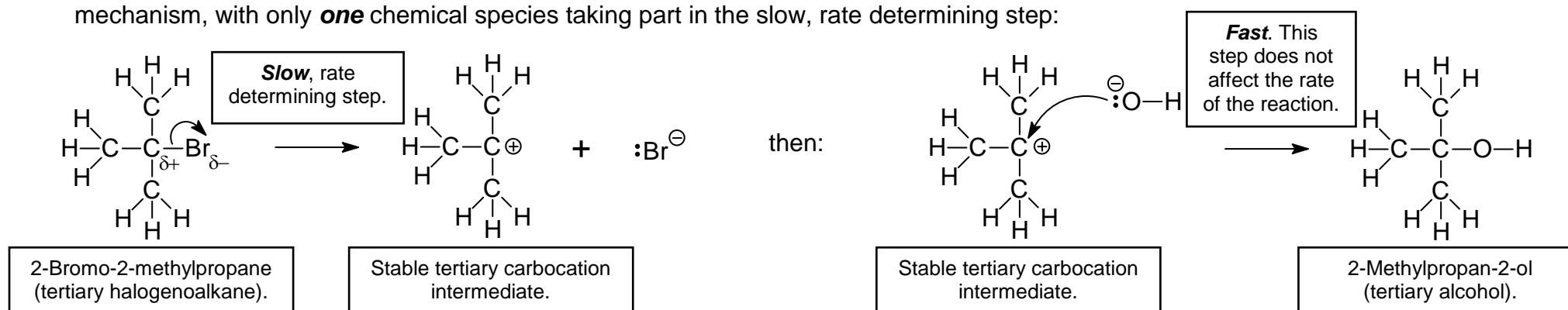
Nucleophilic Substitution into Halogenoalkanes

The S_N1 Reaction Mechanism for Tertiary Halogenoalkanes

An example of a tertiary halogenoalkane is 2-bromo-2-methylpropane. When 2-bromo-2-methylpropane is refluxed with an aqueous solution of sodium hydroxide, the nucleophilic hydroxide ion substitutes the bromine of the tertiary halogenoalkane to form the tertiary alcohol 2-methylpropan-2-ol:



The reaction takes place via an **S_N1** reaction mechanism. This means that the reaction takes place via a **nucleophilic substitution** mechanism, with only **one** chemical species taking part in the slow, rate determining step:



Initially, the carbon-to-bromine covalent bond of the tertiary halogenoalkane breaks to form a tertiary carbocation and a bromide ion. This is the slowest stage of the reaction and it therefore controls the overall rate of the reaction. Because only the tertiary halogenoalkane is involved in the slow, rate determining stage of the reaction, only changing the concentration of the tertiary halogenoalkane will affect the rate of the reaction. The hydroxide ions are not involved in the slow, rate determining step and so changing the concentration of the hydroxide ions will not affect the rate of the reaction.

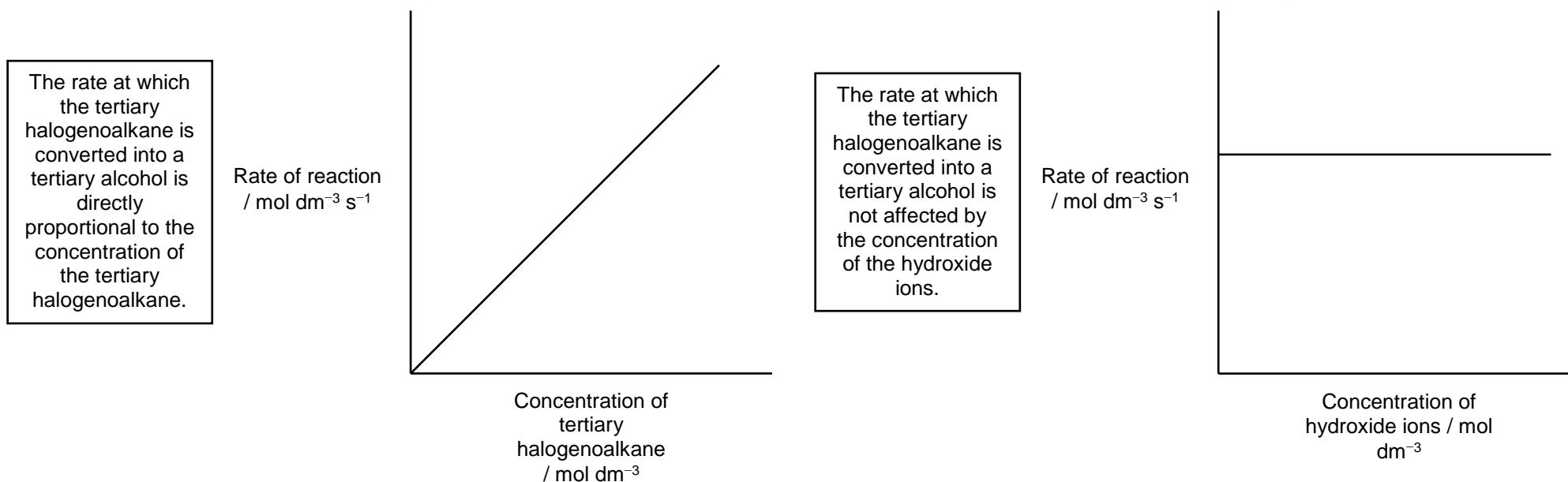
The rate expression for this reaction is written as:

$$\text{Rate} = k \times [\text{tertiary halogenoalkane}]^1 \times [\text{OH}^-]^0 \text{ (first order with respect to the tertiary halogenoalkane and zero order with respect to the hydroxide ions)}$$

Because $[\text{OH}^-]^0 = 1$ the rate expression for the reaction can be simplified to:

$$\text{Rate} = k \times [\text{tertiary halogenoalkane}]^1$$

The rate at which the tertiary halogenoalkane is converted into a tertiary alcohol is therefore **directly proportional** to the concentration of the tertiary halogenoalkane, but it is not affected by the concentration of hydroxide ions (see graphs below):



The tertiary carbocation intermediate that is formed during the reaction is stabilised by the electron donating effect, or **inductive effect**, of the three methyl groups towards the central positively charged carbon. It is due to the stability of the tertiary carbocation that tertiary halogenoalkanes react by an S_N1 mechanism. By comparison, primary carbocations are unstable (because there is only one methyl group present to stabilise the positively charged carbon) and so primary halogenoalkanes do not react by an S_N1 mechanism, but instead react by a different S_N2 mechanism. Finally, because opposite charges attract, the negative hydroxide ion is attracted towards the positive carbocation to form a tertiary alcohol.

A' Level Examination Question

- (a) Bromoalkanes may be hydrolysed, using aqueous sodium hydroxide, to form alcohols either by an S_N1 or an S_N2 mechanism. Explain what is meant by the terms S_N1 and S_N2 .

S_N1

S_N2

(2 marks)

- (b) **Table 1** contains data relating to the hydrolysis of two bromoalkanes, **X** and **Y**, using aqueous sodium hydroxide.

Hydrolysis of X			Hydrolysis of Y		
Rate / mol dm ⁻³ s ⁻¹	[X] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³	Rate / mol dm ⁻³ s ⁻¹	[Y] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³
1.71×10^{-5}	0.10	0.10	1.01×10^{-3}	0.10	0.10
3.42×10^{-5}	0.20	0.10	2.02×10^{-3}	0.20	0.10
6.84×10^{-5}	0.20	0.20	2.02×10^{-3}	0.20	0.20
2.73×10^{-4}	0.40	0.40	4.04×10^{-3}	0.40	0.40

Table 1

Use the data from **Table 1** to predict the type of mechanism (S_N1 or S_N2) involved in the hydrolyses of the bromoalkanes **X** and **Y**. Explain your prediction.

Predicted mechanism for the hydrolysis of X

Explanation

Predicted mechanism for the hydrolysis of Y

Explanation

(6 marks)

- (c) Bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, and 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, are both bromoalkanes.
- (i) Predict which of these bromoalkanes is more likely to be hydrolysed by an $\text{S}_{\text{N}}1$ mechanism and explain your prediction.

Prediction

Explanation

.....

(3 marks)

- (ii) Using the bromoalkane predicted in (c)(i), outline a mechanism for its $\text{S}_{\text{N}}1$ hydrolysis by aqueous sodium hydroxide.

(3 marks)

Answer to the A' Level Examination Question

- (a) **S_N1** A nucleophilic substitution reaction in which only **one** chemical species takes part in the slow rate determining step.
- S_N2** A nucleophilic substitution reaction in which **two** different chemical species take part in the slow rate determining step.

(b) The Information given in the question for the hydrolysis of bromoalkane **X** is reproduced below:

Hydrolysis of X			
Rate / mol dm ⁻³ s ⁻¹	[X] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³	
1.71 × 10 ⁻⁵	0.10	0.10	Experiment 1
3.42 × 10 ⁻⁵	0.20	0.10	Experiment 2
6.84 × 10 ⁻⁵	0.20	0.20	Experiment 3
2.73 × 10 ⁻⁴	0.40	0.40	Experiment 4

Rate doubles as the concentration of bromoalkane **X** doubles.

Rate doubles as the concentration of OH⁻ doubles.

Compare the data from experiments 1 and 2. The concentration of bromoalkane **X** doubles from experiment 1 to experiment 2 (0.10 to 0.20 mol dm⁻³), but the concentration of OH⁻ remains unchanged (0.1 mol dm⁻³). Therefore, any change in the rate of reaction is **only** due to a change in the concentration of bromoalkane **X**. As the concentration of bromoalkane **X** **doubles** (0.10 to 0.20 mol dm⁻³) so the rate of reaction **doubles** (1.71 × 10⁻⁵ to 3.42 × 10⁻⁵ mol dm⁻³ s⁻¹). This demonstrates that bromoalkane **X** takes part in the rate determining step of the reaction.

Compare the data from experiments 2 and 3. The concentration of OH⁻ doubles from experiment 2 to experiment 3 (0.10 to 0.20 mol dm⁻³), but the concentration of bromoalkane **X** remains unchanged (0.2 mol dm⁻³). Therefore, any change in the rate of reaction is **only** due to a change in the concentration of OH⁻. As the concentration of OH⁻ **doubles** (0.10 to 0.20 mol dm⁻³) so the rate of reaction **doubles** (3.42 × 10⁻⁵ to 6.84 × 10⁻⁵ mol dm⁻³ s⁻¹). This demonstrates that OH⁻ takes part in the rate determining step of the reaction.

Both bromoalkane **X** and OH⁻ take part in the rate determining step, so the hydrolysis of bromoalkane **X** takes place by an **Sn2** reaction mechanism.

The Information given in the question for the hydrolysis of bromoalkane **Y** is reproduced below:

Hydrolysis of Y			
Rate / mol dm ⁻³ s ⁻¹	[Y] / mol dm ⁻³	[OH ⁻] / mol dm ⁻³	
1.01 × 10 ⁻³	0.10	0.10	Experiment 1
2.02 × 10 ⁻³	0.20	0.10	Experiment 2
2.02 × 10 ⁻³	0.20	0.20	Experiment 3
4.04 × 10 ⁻³	0.40	0.40	Experiment 4

Rate doubles as the concentration of bromoalkane **Y** doubles.

Rate remains unchanged as the concentration of OH⁻ doubles.

Compare the data from experiments 1 and 2. The concentration of bromoalkane **Y** doubles from experiment 1 to experiment 2 (0.10 to 0.20 mol dm⁻³), but the concentration of OH⁻ remains unchanged (0.1 mol dm⁻³). Therefore, any change in the rate of reaction is **only** due to a change in the concentration of bromoalkane **Y**. As the concentration of bromoalkane **Y** **doubles** (0.10 to 0.20 mol dm⁻³) so the rate of reaction **doubles** (1.01 × 10⁻³ to 2.02 × 10⁻³ mol dm⁻³ s⁻¹). This demonstrates that bromoalkane **Y** takes part in the rate determining step of the reaction.

Compare the data from experiments 2 and 3. The concentration of OH⁻ doubles from experiment 2 to experiment 3 (0.10 to 0.20 mol dm⁻³), but the concentration of bromoalkane **Y** remains unchanged (0.2 mol dm⁻³). Therefore, any change in the rate of reaction is **only** due to a change in the concentration of OH⁻. As the concentration of OH⁻ **doubles** (0.10 to 0.20 mol dm⁻³) the rate of reaction **remains unchanged** (2.02 × 10⁻³ mol dm⁻³ s⁻¹). This demonstrates that OH⁻ does not take part in the rate determining step of the reaction.

Only bromoalkane **Y** takes part in the rate determining step, so the hydrolysis of bromoalkane **Y** takes place by an **S_N1** reaction mechanism.

(c)

(i) The bromoalkane 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, will be hydrolysed by an $\text{S}_{\text{N}}1$ reaction mechanism.

2-Bromo-2-methylpropane is a tertiary halogenoalkane. Tertiary halogenoalkanes react to form stable tertiary carbocations.

Tertiary carbocations are stabilised by the electron donating effect (inductive effect) of the attached methyl groups.

(ii)

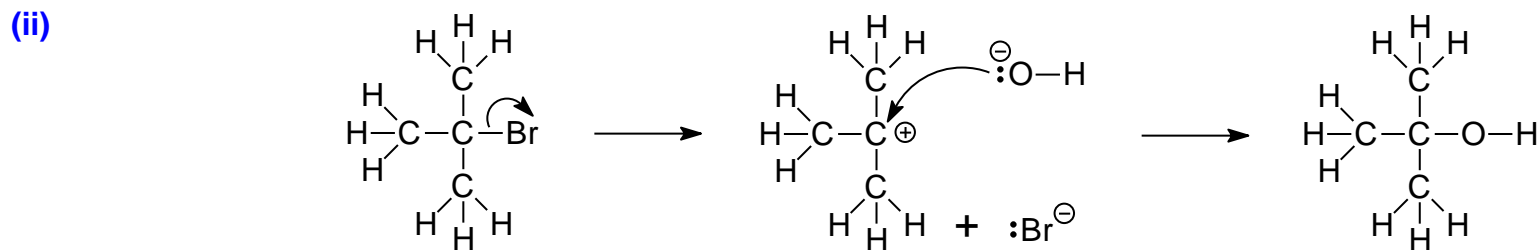


Mark Scheme for the A' Level Examination Question

- (a) **S_N1** nucleophilic substitution / one species in rate determining step
S_N2 nucleophilic substitution / two species in rate determining step
 (1 mark) (1 mark)
- (b) *Predicted mechanism for the hydrolysis of X* S_N2 (1 mark)
Explanation rate dependent* on [X] **or** 1st order with respect to X (1 mark)
 rate dependent* on [OH⁻] **or** 1st order with respect to OH⁻ (1 mark)
Predicted mechanism for the hydrolysis of Y S_N1 (1 mark)
Explanation rate dependent* on [Y] **or** 1st order with respect to Y (1 mark)
 rate not dependent* on [OH⁻] **or** zero order with respect to OH⁻ (1 mark)

* the term *dependent* must be qualified, e.g. “directly proportional to” or “double [X] → double rate”

- (c)
 (i) *Prediction* 2-bromo-2-methylpropane **or** (CH₃)₃CBr (1 mark)
Explanation forms a more stable tertiary carbocation (1 mark)
 because of inductive effect **or** electron movement from CH₃ groups (1 mark)



- electron movement towards Br in the C – Br bond as shown by the correct curved arrow (1 mark)
 correct structure for the tertiary carbocation (1 mark)
 attack by OH⁻ on the positive carbon of the tertiary carbocation as shown by the correct curved arrow (1 mark)