Chem Factsheet

April 2003 Number 49

Rate Orders and Mechanisms of Chemical Reactions

Before working through this Factsheet you should:
- understand the principles of kinetics covered so far at AS and A2 (Factsheets 10, 43 and 44).
- ensure you are fully competent in writing rate expressions and finding orders of reactions.

After working through this Factsheet you will be able to:
- identify the mechanism for the nucleophilic substitution of halogenoalkanes by hydroxide ions from the rate expression and its order;
- write the two mechanisms for nucleophilic substitution and be able to explain how each type gives rise to its rate order;
- recognise which halogenoalkane is likely to undergo which type of mechanism;
- quote the Arrhenius Equation and explain its use in reaction kinetics.

Reaction kinetics

1. The balanced (stoichiometric) chemical equation can tell you nothing about how fast or how slow (kinetics) the reaction will proceed – it has to be from **experiments** using the reactants.
2. The **data** from experiments is obtained by measuring the 'initial rate' whilst varying the concentrations (mol dm^{-3}) of the reactants.
3. Only the reactants involved in the **slowest** step (the 'rate determining step') appear in the **rate expression.**
4. The rate expression is of the form

$$\text{rate} = k \times [A]^a \times [B]^b$$

- k = rate constant
- a and b are called 'orders'
- a + b = 'overall order' of the reaction
- the **units** of k need to be worked out for each expression

(rate units = mol dm^{-3}s^{-1}, [ ] = mol dm^{-3})

5. At A2 level 'orders' are 0,1 or 2 only.
6. The Maxwell-Boltzmann curve shows that increasing the temperature speeds up the rate of reaction, not just because the number of collisions increase (particles moving faster) but more of the particles have the minimum energy (activation energy = E_A) to produce a reaction when they do collide.

Exam Hint - The reason that this Factsheet concentrates only on 'nucleophilic substitution of halogenoalkanes' is because it is the quoted example in A2 specifications.

Beware – you may be presented with examples that do not look like 'halogenoalkanes' – remember they will always fit the principles shown in this Factsheet for halogenoalkanes for SN1 and SN2.

Note SN1 = 'substitution, nucleophilic, 1st order'
SN2 = 'substitution, nucleophilic, 2nd order'

'nucleophilic substitution' reactions/mechanisms

Substitution - when an atom/group in a molecule is removed and then replaced by another atom/group. **Basically – 'swapping parts'**.

Nucleophile - 'a donor of a lone pair of electrons'. Basically – 'nucleophile' means 'positive liking' (the nucleus is positive). Nucleophiles are often (not always) negatively charged, so are attracted to anions (+) or polarised atoms (δ+)

Mechanisms - ↷ represents the movement of a pair of electrons when writing mechanisms.

$C^{\delta+}$—$Br^{\delta-}$ shows Br is more **electronegative** than C so attracts the electron bonding pair towards itself, hence producing a **dipole** (δ+/δ-) and a **polar bond.**

Homolytic fission of a covalent bond

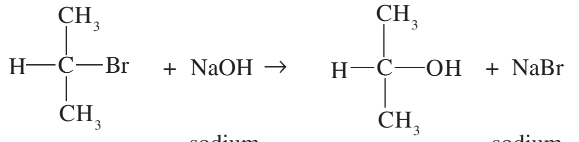
e.g. C—X → C$^{\bullet}$+ X$^{\bullet}$ producing **free radicals**
(one electron to each atom)

Heterolytic fission of a covalent bond

e.g. C—X → C$^{\oplus}$ + X$^{\ominus}$producing **ions**
(both electrons move to one of the two atoms).

Nucleophic substitution of halogenoalkanes and the order of reaction

When aqueous sodium hydroxide solution is added to a halogenoalkane a nucleophilic substitution reaction takes place. The halogen atom (Cl/Br/I) is replaced by a hydroxide group (OH).



$$\text{H—C(CH}_3\text{)}_2\text{—Br} + \text{NaOH} \rightarrow \text{H—C(CH}_3\text{)}_2\text{—OH} + \text{NaBr}$$

2-bromopropane + sodium hydroxide → propan-2-ol + sodium bromide

N.B. OH^- is the nucleophile.

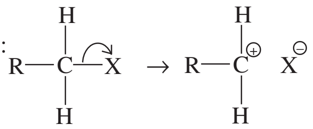
This reaction is written in its general form as:

$$R—X + OH^- \rightarrow R—OH + X^-$$

There are two ways in which this reaction could take place (the 'mechanisms').

Mechanism 1

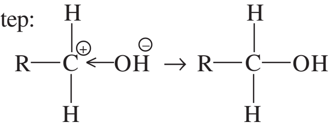
First step:



$$R—CH_2—X \rightarrow R—CH_2^{\oplus} \quad X^{\ominus}$$

This is **heterolytic fission** of the C—X bond forming the carbocation and the halide ion. This is the **SLOW STEP**

Second step:



$$R—CH_2^{\oplus} \leftarrow OH^{\ominus} \rightarrow R—CH_2—OH$$

The **nucleophile** (OH^-) forms a covalent bond with the carbocation by donating a lone pair of electrons. This is the **FAST STEP**

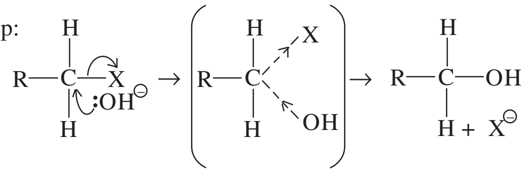
Since the **slowest step** is the **rate determining step,** only the halogenoalkane is involved in the rate expression. So it will be of the form:

$$\boxed{\text{rate } k \times [RCH_2 – X]}$$

This **FIRST ORDER** – so this mechanism is **SN1**

Mechanism 2

First step:



In this mechanism the nucleophile forms the covalent bond as the heterolytic fission is taking place.

The transition state shows both the incoming OH and the leaving X 'in contact' with the carbon atom at one point in time.

The **transition state** is the **rate determining step** and since both the halogenoalkane and the $OH^{\ominus}$ are involved they appear in the rate expression. So it will be of this form:

$$\boxed{\text{rate} = k \times [RCH_2 - X] \times [OH^{\ominus}]}$$

This is the **SECOND ORDER** - so the mechanism is **SN2**

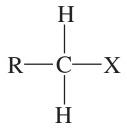
SN1 - the mechanism is in **TWO STEPS**
- rate = $k \times$ [halogenoalkane]

SN2 - the mechanism involved a **TRANSITION STAGE**
- rate = $k \times$ [halogenoalkane] $\times$ $[OH^-]$

***Exam Hint** - Questions on this topic usually follow this format:*
(a) using experimental data to write the rate expression
(b) asking what the rate expression tells you about the mechanism
(c) asking you to draw and explain the mechanism

Which halogenoalkanes use which mechanism?

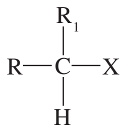
Primary Halogenoalkanes



$R\text{—}CH_2\text{—}X$

SN2

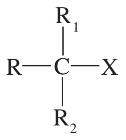
Secondary Halogenoalkanes



$R\text{—}C(R_1)(H)\text{—}X$

may be SN1 or SN2 or a mixture of both

Tertiary Halogenoalkanes



$R\text{—}C(R_1)(R_2)\text{—}X$

SN1

Remember this is a **general rule** – only the experimental data giving the order ensures which mechanism it will be.

NB. The choice of mechanism is decided by the **stability of the carbocation.**

Tertiary halogenoalkanes form more stable carbocations so Mechanism 1 where the carbocation is formed is the most likely for them.
Primary halogenoalkanes usually go via the transition state because their carbocations are less stable.

The Arrhenius Equation

At this level you need to know that following facts:

Increasing the **temperature** increased the **rate of reaction** by increasing the **rate constant**:

$$k = Ae^{-\frac{E_A}{RT}}$$

k = rate constant
E_A = activation energy
T = temperature in degrees Kelvin (273 + °C)
R = the gas constant (8.31 $JK^{-1}\ mol^{-1}$)
A = a constant
e = a number that goes on for ever (like π)
It is about 2.72

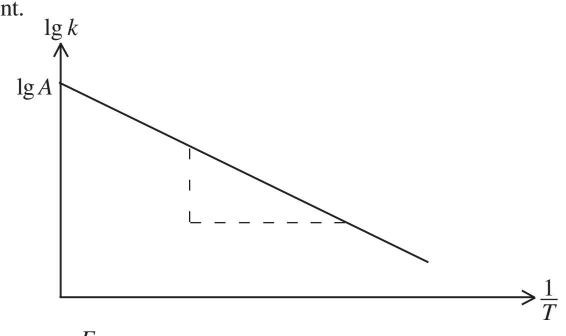
The equation can be re-written as:

$$\lg k = \lg A - \frac{E_A}{2.303R}\left(\frac{1}{T}\right)$$

This fits the equation for a straight line:

y = c + mx

If you plot lg$k$ against $\frac{1}{T}$ you will obtain a straight line with a negative gradient.



$$\text{gradient} = \frac{-E_A}{2.303R}$$

This enables you to calculate a value for E_A.the activation energy.

Questions

1. The following data were obtained for the reaction:

$R\text{—}Br + OH^- \rightarrow R\text{—}OH + Br^-$

Experiment	Initial concentrations/mol dm^{-3} RBr	OH^-	Initial rate/ mol $dm^{-3}s^{-1}$
1	0.1	0.4	3.0×10^{-3}
2	0.2	0.4	6.0×10^{-3}
3	0.1	1.6	1.2×10^{-2}

(a) What is the order of reaction with respect to
 (i) RBr?
 (ii) OH^-?

(b) Write the rate expression for the reaction.

(c) Calculate the value of the rate constant.

(d) (i) What does the rate expression tell you about the mechanism of the reaction?
 (ii) Draw and explain the mechanism you stated in part (i).

2. The following data were obtained for the reaction:

$R\text{—}I + OH^- \rightarrow R\text{—}OH + I^-$

Experiment	Initial concentrations/mol dm^{-3} RI	OH^-	Initial rate/ mol $dm^{-3}s^{-1}$
1	0.2	0.2	2.4×10^{-2}
2	0.4	0.2	4.8×10^{-2}
3	0.2	0.4	2.4×10^{-2}

(a) What is the order of reaction with respect to
 (i) RI?
 (ii) OH^-?

(b) Write the rate expression for the reaction.

(c) Calculate the value of the rate constant.

(d) (i) What does the rate expression tell you about the mechanism of the reaction?
 (ii) Draw and explain the mechanism you stated in part (i).

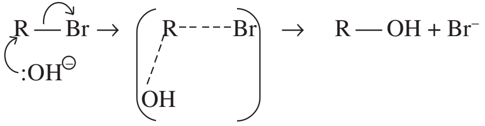
Answers

1. (a) (i) 1
   (ii) 1

   (b) rate = k × [RBr] × $[OH^-]$
   (c) 0.075 $mol^{-1}\ dm^3 s^{-1}$

   (d) (i) Because it is 2nd order overall it must go via a mechanism involving a transition state i.e. both RBr and OH^- are in the rate determining step.

   (ii)



As the OH^- (nucleophile) donates a lone pair the Br comes away through heterolytic fission. At a moment in time both will be in contact with the carbon atom so forming the transition state.

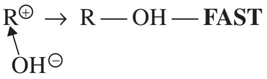
2. (a) (i) 1
   (ii) 0

   (b) rate = $k \times [RI]$

   (c) 0.12 s^{-1}

   (d) (i) Only RI appears in the rate expression so only RI is in the rate determining step.
   This means that it is a 2 step mechanism.

   (ii) $R — I \rightarrow R^{\oplus} + I^{\ominus}$ — **SLOW**
   (formation of the carbocations by heterolytic fission)
   This is the rate determining step.



$R^{\oplus} \rightarrow R — OH$ — **FAST**
$OH^{\ominus}$

(nucleophile donating a lone pair of electrons to form a covalent bond).

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