ChemFactsheet

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Reaction Mechanisms - Revision Summary

Before working through this factsheet you should:
- Have a good understanding of electronegativity and bond polarity;
- Have a good knowledge of bond fission;
- Have read Factsheets 40 (reaction mechanisms) and 52 (reactions of functional groups – a summary).

After working through this factsheet you will:
- Have been shown the relationship between bond polarity and bond breaking;
- Have been given an explanation of which substances react by which mechanism;
- Be able to suggest a mechanism for an unknown reaction.

Substitution Reactions

Substitution reactions involve bond breaking, then bond forming.

$CH_3CH_2Cl + NaOH \rightarrow CH_3CH_2OH + NaCl$

A C-Cl bond breaks, then a C-OH bond forms.

Breaking a covalent bond can happen in two ways:

1. *Homolytic fission* where each fragment retains one of the bonding electrons and ***free radicals*** are formed.
   In thermal cracking
   $CH_3(CH_2)_{10}–(CH_2)_8CH_3 \rightarrow CH_3(CH_2)_{10}^{\bullet} + CH_3(CH_2)_8^{\bullet}$

2. ***Heterolytic fission*** where one fragment retains **both** bonding electrons. **Positive and negative *ions*** are formed.
   $C_{11}H_{23}–C_9H_{19} \rightarrow C_{11}H_{23}^{+} + C_9H_{19}^{-}$

The **type** of fission depends on ***bond polarity***.

Non-polar bonds are present in diatomic molecular elements (eg the Cl-Cl bond in Cl_2) and symmetrical molecules (eg the C-H bonds in alkanes).
- There is an **equal** sharing of electrons between atoms.
- On breaking, there is no tendency for the two electrons to go with one atom rather than the other
- **free radicals** are formed by homolytic fission.

Polar bonds are formed between atoms of different **electronegativities.**
- One atom attracts the bonding pair of electrons **more** than the other.
- On breaking, **ions** are formed by heterolytic fission.

The term used to define a reaction mechanism indicates
1. **the type of reaction, and**
2. **the instigator of the reaction.**

Free radical substitution

Involves the formation of free radicals from a molecule in the **initiation** stage.

$Cl_2 \rightarrow 2Cl^{\bullet}$

This is followed by **propagation** which involves two reactions, both of which involve a free radical colliding with a molecule to give **another** free radical and molecule.

$Cl^{\bullet} + CH_4 \rightarrow HCl + CH_3^{\bullet}$
$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$
Radical Molecule Molecule Radical

Two free radicals collide to form a molecule in the **termination** stage.

$CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$
$2CH_3^{\bullet} \rightarrow C_2H_6$
2 Radicals 1 Molecule

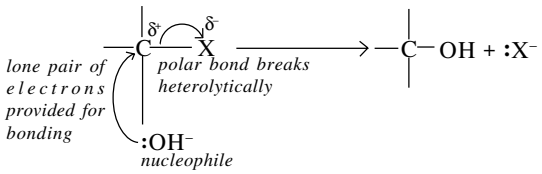
The instigator is the chlorine **radical**; the type of reaction is **substitution**. The mechanism is ***free radical substitution***.

Nucleophilic substitution

Polar bonds in halogenoalkanes and alcohols **produce $C^{\delta+}$**.

(X is a halogen atom)

$C^{\delta+}$ is susceptible to attack from a *nucleophile* which approaches this *electron-deficient* site. The bond breaks **heterolytically** and the lone pair of electrons on the nucleophile forms a new bond.



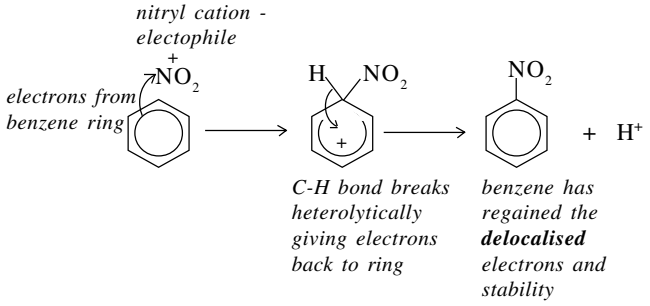
The instigator is OH^-, the **nucleophile**. The type of reaction is **substitution**. The mechanism is *nucleophilic substitution*.

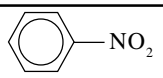
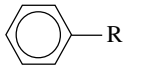
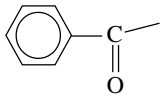
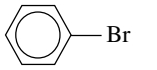
Note: that when X or OH is attached directly to a benzene ring, nucleophilic substitution does **not** take place. The bonds are too strong.

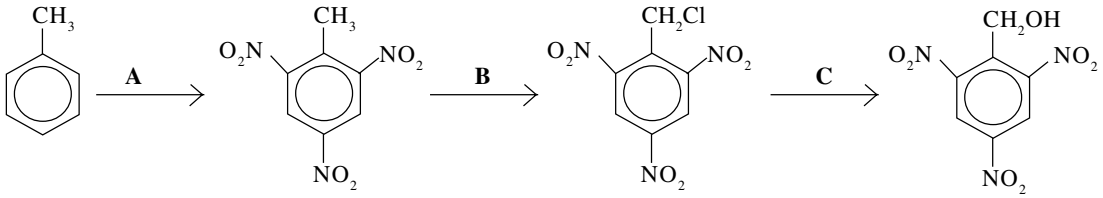
Reactant	Bond Broken	Nucleophile	Bond Formed	Products
halogenalkane	C–X	$:OH^-$ $:NH_3$ $:CN^-$	C–OH C–NH_2 C–CN	alcohol amine nitrile
alcohol	C–OH	$:X^-$	C–X	halogenoalkane

Electrophilic substitution

The π-bonding in benzene involving delocalised electrons above and below the benzene ring means that this *negative charge density* **repels** nucleophiles but attracts **electrophiles** (*electron-deficient* species).



Electrophile	Bond Formed	Product
NO_2^+		nitrobenzene
R^+ (alkyl)		an alkylbenzene (e.g. methylbenzene)
RCO^+ (acyl)		a ketone
Br^+		Bromobenzene

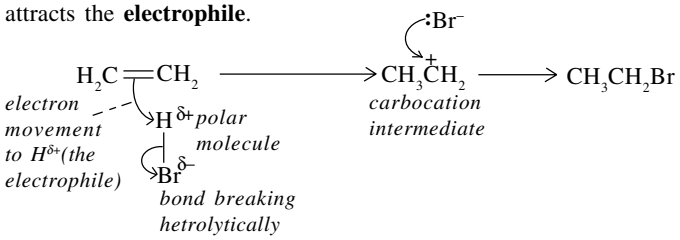


Reaction	Bond broken	Bond formed	Substitution mechanism
A	C–H of benzene	C–NO_2	electrophilic
B	C–H of methyl group	C–Cl	free radical
C	C–Cl (polar bond)	C–OH	nucleophilic

Addition Reactions

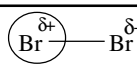
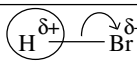
In an addition reaction, **two** molecules add together to give **one** molecule.

In **alkenes**, the π-bonding of the C=C bond involves *negative charge density* above and below the bond. This **repels** the nucleophile but attracts the **electrophile**.

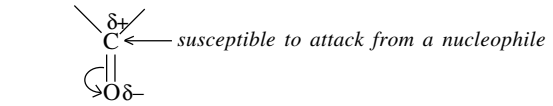


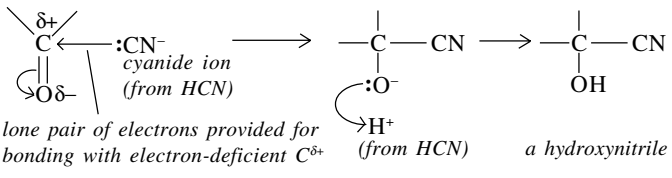
The instigator is the **electrophile**, $H^{\delta+}$ of H–Br. It is an **addition** reaction. The mechanism is *electrophilic addition*.

Addition to RCH=CH_2

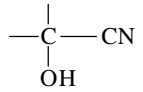
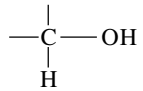
Molecule added	Electrophile	Product(s)
Br_2		$RCHBrCH_2Br$ a dihalogenoalkane
HBr		$RCHBrCH_2$ + RCH_2CH_2Br (major) (minor) halogenoalkanes
H_2O	H^+	$RCH(OH)CH_3$ + RCH_2CH_2OH (major) (minor) alcohols

In *aldehydes* and *ketones*, the **carbonyl** group, C=O is **polar**.





The **nucleophile**, CN^- is the instigator. It attacks the $C^{\delta+}$ of the C=O. It is an **addition** reaction. The mechanism is **nucleophilic addition.**

Added	Nucleophile	Product(s)
HCN	$:CN^-$ from HCN	 *a hydroxynitrile*
2H atoms	$:H^-$ from $NaBH_4$	 *an alcohol*

Elimination Reactions

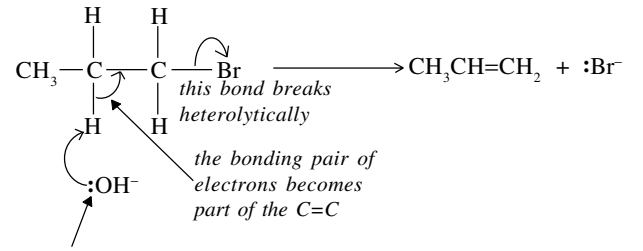
In an elimination reaction, **one** molecule becomes **two** molecules. It is the opposite of addition.

In *halogenoalkanes*, hydrogen halide is eliminated across **adjacent** carbon atoms. This is *dehydrohalogenation*.

Elimination of HBr across carbons 1 and 2

$CH_3\overset{2}{C}H_2\overset{1}{C}H_2Br \longrightarrow CH_3CH{=}CH_2 + HBr$

1- bromopropane *propene*



*behaves as a **base** extracting a proton, H^+*

$CH_3\overset{1}{C}H\overset{2}{C}l\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

2-chloropentane

$CH_2\overset{1}{=}\overset{2}{C}HCH_2CH_2CH_3$

pent-1-ene

elimination of HCl across carbons 1 and 2

$CH_3\overset{2}{C}H\overset{3}{=}CHCH_2CH_3$

pent-2-ene

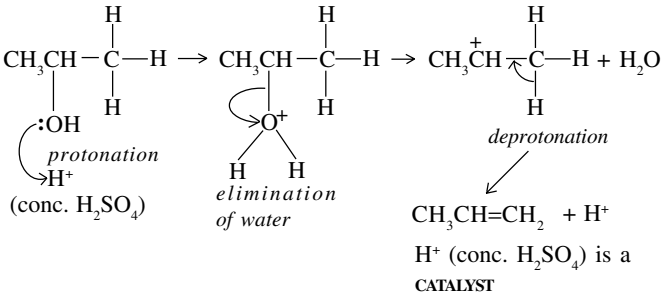
elimination of HCl across carbons 2 and 3

Both products are formed

In **alcohols**, water is eliminated across adjacent carbon atoms. This is *dehydration*.

$CH_3\overset{1}{C}H(OH)\overset{2}{C}H_3\overset{3}{} \longrightarrow CH_3CH{=}CH_2 + H_2O$

propan-2-ol propene



$CH_3CH{=}CH_2 + H^+$

H^+ (conc. H_2SO_4) is a **CATALYST**

$CH_3CH_2CH_2CH(OH)CH_3$

pentan-2-ol

$CH_3CH_2CH_2\overset{2}{C}H\overset{1}{=}CH_2$

pent-1-ene

elimination of H_2O across carbons 1 and 2

$CH_3\overset{2}{C}H\overset{3}{=}CHCH_2CH_3$

pent-2-ene

elimination of H_2O across carbons 2 and 3

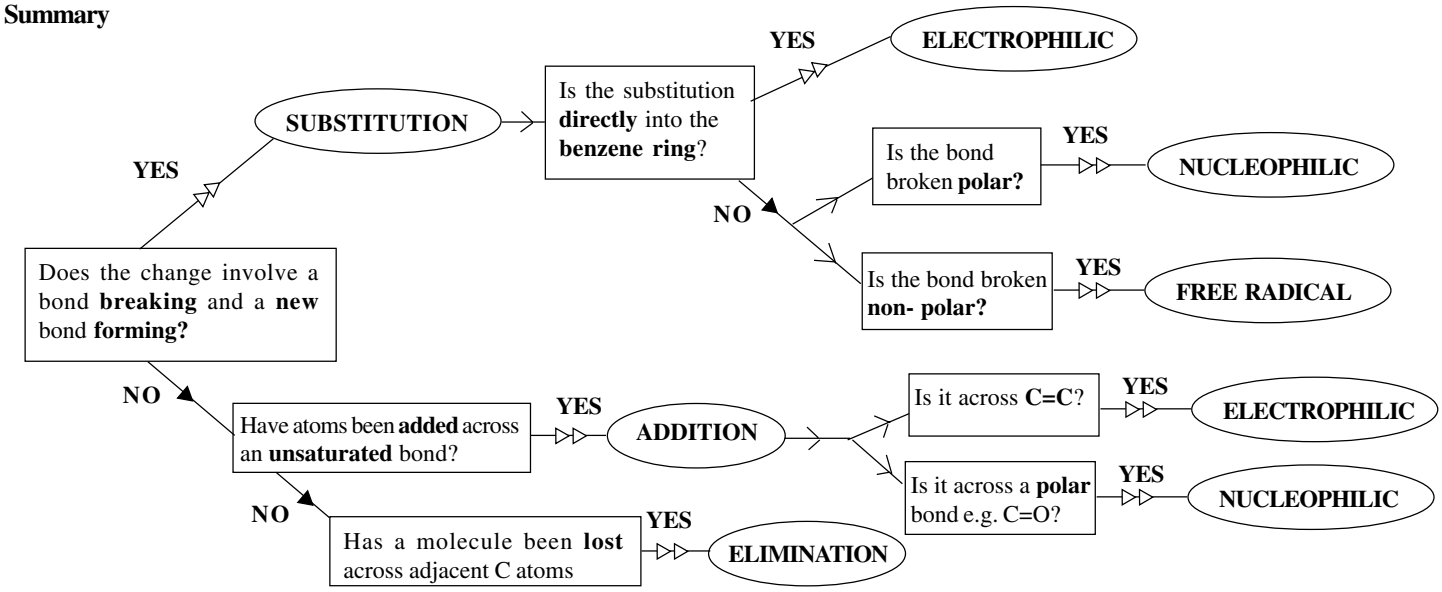
Both products are formed

Note that both these reaction mechanisms are described simply as **elimination**. No indication is needed as to the instigator of the reaction.

Exam Hint: *Do not be put off by the complexity of an organic molecule. Organic chemistry is the chemistry of **functional groups**. In order to identify a mechanism:*

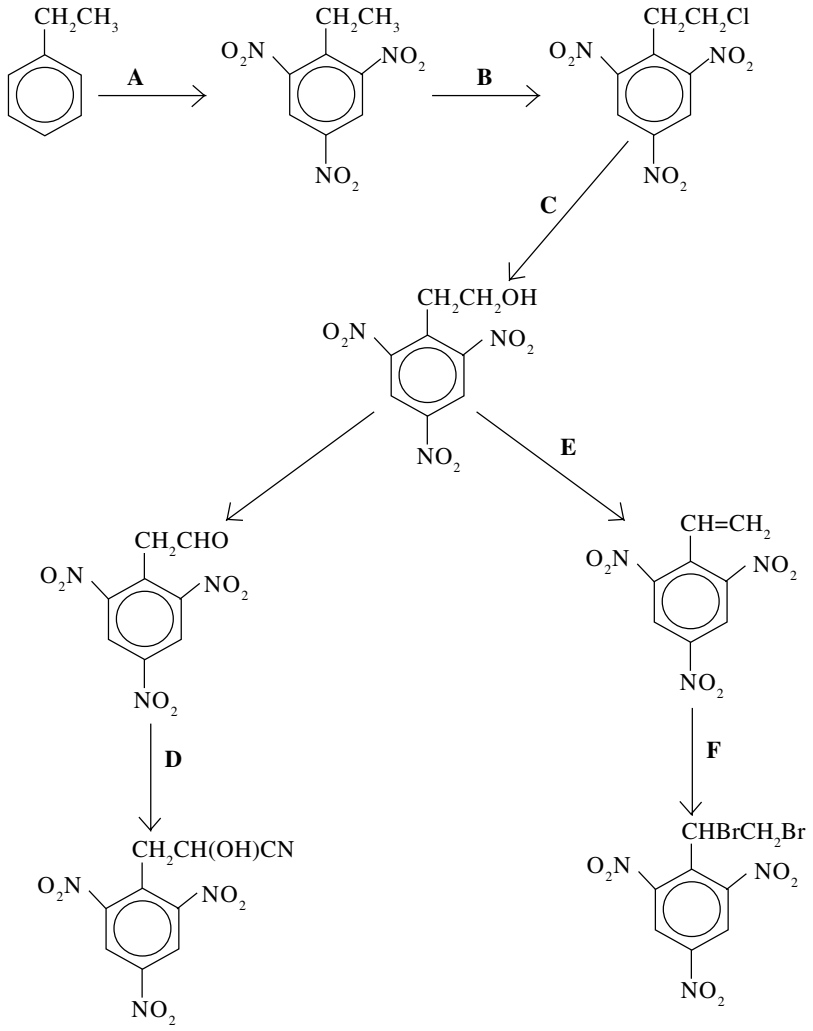
1. *Identify the difference between reactant and product,*
2. *Decide whether substitution, addition or elimination has taken place,*
3. *Identify the instigator – free radical, electrophile or nucleophile (<u>not</u> elimination),*
4. *Now you can describe the mechanism.*

Summary



Questions

1. Identify the mechanisms, A to F, in the following reaction sequence:

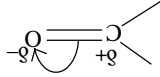


2. Which **one** of the following products is formed when but-2-enal, $CH_3CH{=}CHCHO$ reacts with $NaBH_4$ (H^-)?
   a) $CH_3CH_2CH_2CHO$ b) $CH_3CH{=}CHCH_2OH$ c) $CH_3CH_2CH_2CH_2OH$

Answers

1. A is electrophilic substitution. (*C-H of* ***benzene*** *breaks, C-NO_2 forms*).
   B is free radical substitution. (***Non-polar*** *C-H breaks, C-Cl forms*)
   C is nucleophilic substitution. (***Polar*** *C-Cl breaks, C-OH forms*).
   D is nucleophilic addition. (*HCN is added across* ***polar*** *C=O*)
   E is elimination. (*H_2O is removed forming C=C*)
   F is electrophilic addition. (*Br_2 is added to C=C*)

2. H- is a **nucleophile**. It attacks the electron deficient $C^{\delta+}$ of C=O.



Two H atoms add across the C=O to give the alcohol.
C=C has negative charge density which **repels** the nucleophile, H^-.
Addition across C=C does **not** take place.
The answer is b), $CH_3CH{=}CHCH_2OH$

Acknowledgements: *This Factsheet was researched and written by Derek Swain.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***