Chem Factsheet

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Avoidable Errors in Reaction Mechanism Questions

The aim of this Factsheet is to enable you to score full marks when answering AS questions on reaction mechanisms.

Mechanisms must be written with care: curly arrows, lone pairs, electrical charges and covalent bonds have to be placed correctly to be certain that full marks will be gained. There are usually alternative answers that will gain (full) credit but these are not given since often they are less precise.

We will consider the correct mechanism and then the same mechanism with typical errors.

However, first of all, here are the meanings of some important terms:

1. Types of Reaction

(a) Addition

a chemical reaction in which two (or more) molecules chemically combine to form a single molecule.
e.g. $H_2C{=}CH_2 + H_2 \rightarrow C_2H_6$ (Also a redox reaction.)

(b) Elimination

A chemical reaction involving the removal of a small molecule (e.g. H_2O, HBr) from an organic molecule to leave an unsaturated molecule.
e.g. $CH_3CH_2Br + KOH \rightarrow H_2C{=}CH_2 + KBr + H_2O$
(HBr has been removed from CH_3CH_2Br)

(c) Substitution

A chemical reaction where one atom or group of atoms is replaced by another atom or group of atoms.
e.g. $CH_3Br + KOH \rightarrow CH_3OH + KBr$

2. Attacking species

(a) Electrophile

An electron pair acceptor. e.g. $^+CH_3$. An electrophile attacks an electron rich centre and forms a new covalent bond by accepting a pair of electrons.

(b) Nucleophile

An electron pair donor. e.g. $^-$:CN / :NH_3. A nucleophile donates a lone pair of electrons to an electron deficient atom (δ+) so forming a co-ordinate bond with that centre.

(c) Free radical

An atom or group of atoms with a single unpaired electron. e.g. •CH_3

(d) Base

a proton acceptor. e.g. ^-OH

3. Reaction Mechanisms

A reaction mechanism is a theoretical stepwise description of how a chemical reaction occurs. A mechanism shows what happens to bonding electrons and sometimes, lone pair electrons. It shows which bonds break and which bonds form and often involves an intermediate species.

A curly arrow (↷) shows the movement of an electron pair. The tail is placed at the electron pair (a covalent bond or a lone pair) and the head shows where the electron pair is to be moved (forming a new covalent bond or new lone pair).

A curly half-arrow ("fishhook") (⌒) shows the movement of a single electron. A dot (•) shows a single unpaired electron. The dot should be on the atom which has the missing electron.

The type of reaction mechanism is obtained by combining the type of attacking species with the type of reaction.

As you work through the following examples you will be presented with the "correct" mechanism along with one containing common errors. Try to spot the errors.

(a) Free Radical Substitution

This is involved when halogens, (e.g. Cl_2 and Br_2) react with alkanes in the presence of UV light.

The UV supplies the energy for the homolytic fission of the non-polar halogen covalent bond.

Mechanism: e.g. Monochlorination of Ethane

Step 1. Initiation: $Cl_2 \rightarrow 2Cl\bullet$ (production of free radicals.)

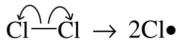
Step 2. Propagation (i) $CH_3CH_3 + Cl\bullet \rightarrow HCl + \bullet CH_2CH_3$

(ii) $Cl_2 + \bullet CH_2CH_3 \rightarrow CH_3CH_2Cl + Cl\bullet$

(Propagation: molecule + free radical → molecule + free radical.)

Step 3. Termination e.g. $2\bullet CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3$

(Combination of two free radicals: stops propagation continuing.)



$Cl—Cl \rightarrow 2Cl\bullet$

(i) $CH_3CH_3 + Cl\bullet \rightarrow HCl + CH_2CH_3\bullet$

(ii) $Cl_2 + CH_2CH_3\bullet \rightarrow C_2H_5Cl + Cl\bullet$

$2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3$

Free radical substitution with errors

Spot the errors and check them at the end of this FactSheet.

(b) Electrophilic Addition

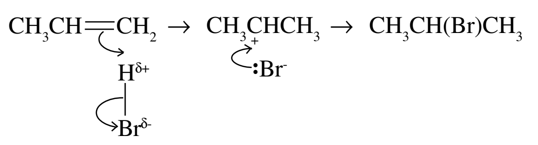
Alkenes have double bonds (>C=C<) and hence, are sites of high electron density. Thus alkenes react with electrophiles provided by such reagents as halogens, (not F_2), hydrogen halides and concentrated sulfuric acid. Addition reactions occur in a two step mechanisms.

- **Step 1:** The pi bond of the double bond breaks with both electrons forming a dative bond with a cation from the attacking electrophile. A carbocation is formed and at the same time an anion.
- **Step 2.** The carbocation combines with the anion by C^+ accepting an electron pair to give the product.

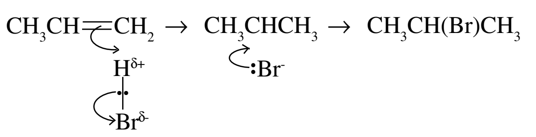
Symmetrical alkenes form only one carbocation and hence only one addition product.

Unsymmetrical alkenes can form two carbocations and hence two products are possible with reagents of the form H-X. The order of stability of carbocations is primary < secondary < tertiary and the more stable the carbocation, the greater yield of the product derived from that carbocation.

Mechanism: e.g. HBr Addition to Propene to Produce 2-bromopropane, the Major Product



$CH_3CH{=}CH_2 \rightarrow CH_3\overset{+}{C}HCH_3 \rightarrow CH_3CH(Br)CH_3$



$CH_3CH{=}CH_2 \rightarrow CH_3CHCH_3 \rightarrow CH_3CH(Br)CH_3$

mechanism with some errors

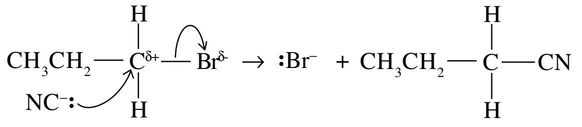
Spot the errors and check them at the end of this FactSheet.

(c) Nucleophilic Substitution

Halogenoalkanes (haloalkanes) have polar bonds ($C^{\delta+}$—$X^{\delta-}$). Hence they react with nucleophiles such $^-$**:**OH, $^-$**:**CN, and **:**NH_3.

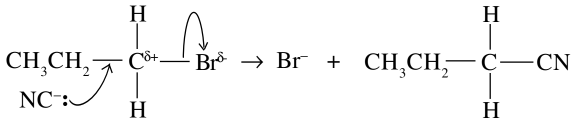
(i) *Primary* halogenoalkanes react by a one step process. Nucleophilic attack on the electron deficient carbon atom ($C^{\delta+}$) and the heterolytic fission of the C-X bond are simultaneous.

Mechanism: e.g. (Sodium) Cyanide in Ethanol with 1-Bromopropane



$CH_3CH_2CH_2^{\delta+}—Br^{\delta-} + NC^- \rightarrow :Br^- + CH_3CH_2CH_2CN$

Note: anion + molecule → anion + molecule



$CH_3CH_2CH_2^{\delta+}—Br^{\delta-} + NC^- \rightarrow Br^- + CH_3CH_2CH_2CN$

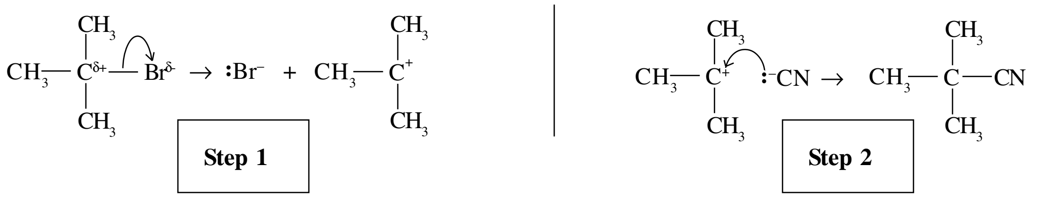
mechanism with some errors

Spot the errors and check them at the end of this FactSheet.

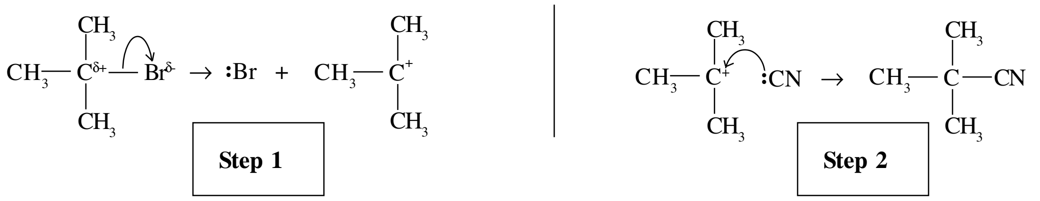
Note The product is butanenitrile. This reaction increases the length of the carbon chain by one carbon atom.

(ii) *Tertiary* halogenoalkanes react by a two step process. Step 1 is the heterolytic fission of the C-X bond producing a carbocation. Step 2 is the rapid combination of the carbocation with the nucleophile.

Mechanism: e.g. (Sodium) Cyanide in Ethanol with 1-Bromo-2-Methylpropane



Note: Tertiary carbocations are able to form because there are three electron donating alkyl groups so spreading this positive charge over the whole ion and so stabilising the ion



mechanism with some errors

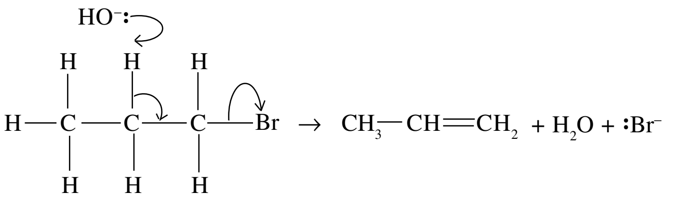
Spot the errors and check them at the end of this FactSheet.

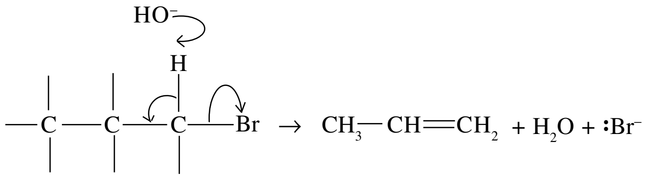
(d) Elimination

Halogenoalkanes (haloalkanes), as well as undergoing nucleophilic substitution reactions with strong alkalis (e.g. KOH and NaOH), can also undergo elimination reactions. The hydroxide ion acts as a Bronsted-Lowry base because it accepts a proton from a carbon atom adjacent to the carbon atom bonded to the halogen atom. Primary halogenoalkanes produce only one alkene.

Some secondary and tertiary halogenoalkanes can produces more than one alkene since the hydrogen atoms on the adjacent carbon atoms are not all equivalent. Elimination is favoured over substitution by using a concentrated ethanolic solution of e.g. KOH. To favour substitution the alkali would be dissolved in water. In both cases heat is usually required.

Mechanism: (Potassium) Hydroxide in Ethanol with 1-Bromopropane





mechanism with some errors

Spot the errors and check them at the end of this FactSheet.

Spotting the Errors in Mechanisms

(a) Free radical substitution

1. Should be "fishhook" arrows (if used at all) in step 1. Also they should originate *from* the bond.
2. In (i), the dot is at wrong end ($CH_2CH_3\bullet$) – electron should be on C of CH_2.
3. In (ii), the dot is at wrong end ($C_2H_5\bullet$) – electron should be on C of CH_2.
4. Dot is missing from line 4 – should be $2\bullet CH_2CH_3$.

(b) Electrophilic addition

1. The H-Br bond should be shown as a line only or electron pair only, not both. This would indicate *4 electrons* between H and Br!
2. The intermediate has no + charge on the central carbon atom.

(c) Nucleophilic substitution

(i) 1. The head of the curly arrow from the cyanide ion should go to the $C^{\text{ä}+}$, not the C-C bond.
  2. The tail of the curly arrow from the C-Br bond must be near the centre of the bond.
  3. The lone pair on Br^- should be shown – these electrons derive from the C-Br bond.

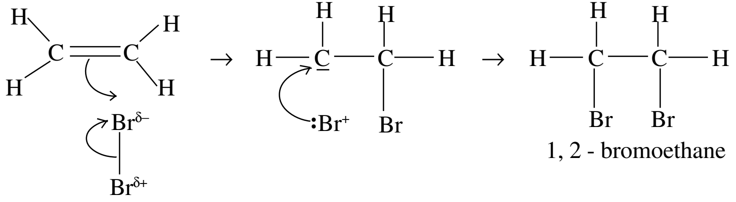
(ii) 1. The charge is missing from the bromide product of step 1.
  2. The charge is missing from the cyanide nucleophile.

(d) Elimination

1. All H atoms should be shown
2. Curly arrow from the negative charge – should be from lone pair.
3. HO^- accepts the wrong proton.
4. Wrong C-H bond moves.

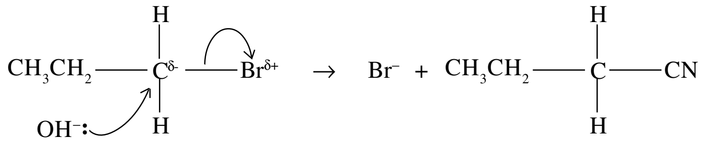
Practice Questions

1. (a) Chloroethane reacts with chlorine in the presence of UV light to form a mixture of products. Write the propagation steps for the conversion of chloroethane into 1,2-dichloroethane.
   (b) A little 1,4-dichlorobutane and also a substance with the empirical formula CH_2Cl are also formed. Write equations for the formation of these products.
2. Write the mechanism for the reaction of concentrated sulfuric acid with propene to produce $CH_3CH(OSO_2OH)CH_3$.
3. Name and outline the mechanism for the conversion of 1-chloropropane into 1-aminopropane by reaction with ammonia.
4. Examine each of the following mechanisms and ***identify the errors*** in each.
   (a) Mechanism of electrophilic addition of Br_2 to ethene



Note: Br_2 is induced by e- being repelled by e- of C=C

(b) Nucleophilic substitution of 1-bromopropane by aqueous hydroxide

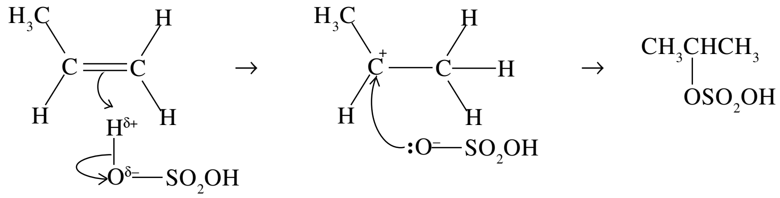


Answers

1. (a) (i) $CH_3CH_2Cl + Cl\bullet \rightarrow HCl + \bullet CH_2CH_2Cl$
   (ii) $Cl_2 + \bullet CH_2CH_2Cl \rightarrow ClCH_2CH_2Cl + Cl\bullet$

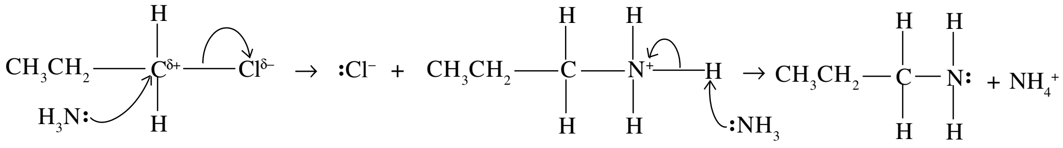
   (b) $2\bullet CH_2CH_2Cl \rightarrow ClCH_2CH_2CH_2CH_2Cl$.
   (c) $\bullet Cl + \bullet CH_2CH_2Cl \rightarrow ClCH_2CH_2Cl$

2.



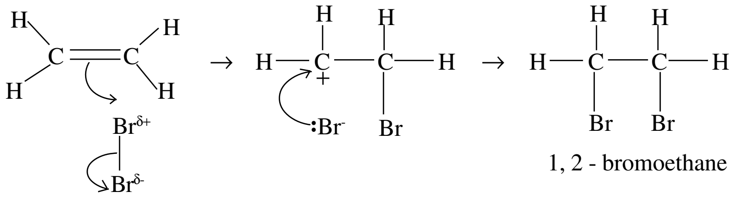
Note: More stable secondary carbocation intermediate is preferred.

3. Nucleophilic substitution



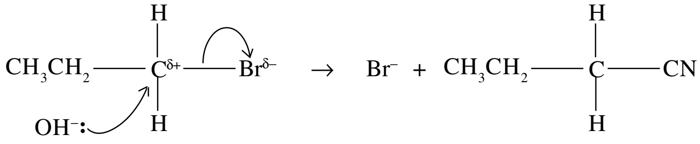
Note: Molecule + molecule → anion + cation (charges must balance). Do not use the **:**Cl^- to act as the base to remove the proton from the cation. Only use NH_3.

4 (a) The induced dipole in bromine is the wrong way round. The intermediate is a carbocation, not a carbanion. The Br is released as a negative ion in the first stage. The cleavage of the Br-Br bond is in the wrong direction. *The correct mechanism follows:*



NB: Br_2 dipole is induced by bond e^- being repelled by e^- of C=C

(b) The lone pair should be on the O of the OH ion. The polarity of the C-Br bond is the wrong way round. A lone pair is missing from the bromide ion product. *The correct mechanism follows:*



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