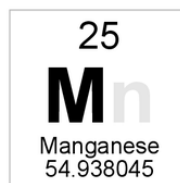
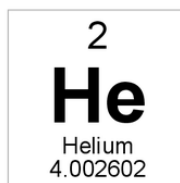
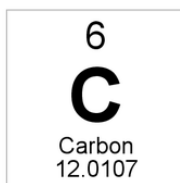
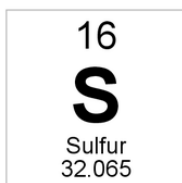
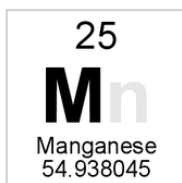


Reactivity 3.4 HL

IB CHEMISTRY HL



Reactivity 3.4.6 / 3.4.7

Understandings:

- A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor (3.4.6).
- When a Lewis base reacts with a Lewis acid, a coordination bond is formed. Nucleophiles are Lewis bases and electrophiles are Lewis acids (3.4.7).

Learning outcomes:

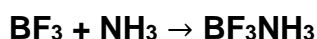
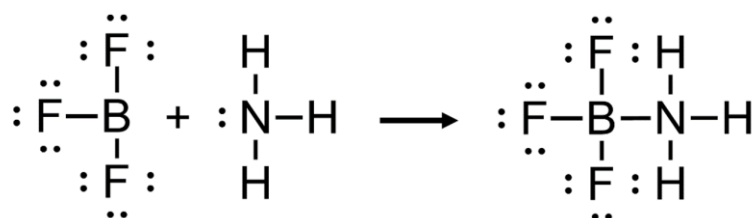
- Apply Lewis acid–base theory to inorganic and organic chemistry to identify the role of the reacting species (3.4.6)
- Draw and interpret Lewis formulas of reactants and products to show coordination bond formation in Lewis acid–base reactions (3.4.7).

Linking question(s):

- Reactivity 3.1 What is the relationship between Brønsted–Lowry acids and bases and Lewis acids and bases?
- Structure 2.2 Do coordination bonds have any different properties from other covalent bonds?

Lewis acids and bases

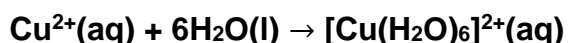
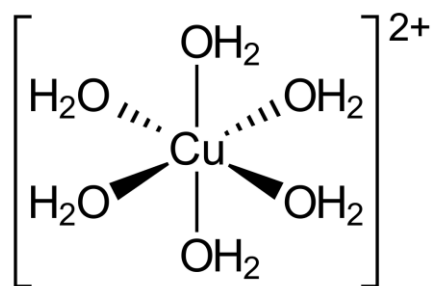
- A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.
- When a Lewis acid and Lewis base react together, the Lewis base donates an electron pair to the Lewis acid.
- A coordination bond is formed between the Lewis acid and the Lewis base.
- Example – BF_3 and NH_3 react together to form BF_3NH_3 .
- NH_3 acts as a Lewis base by donating an electron pair to BF_3 which acts as a Lewis acid by accepting the electron pair.



- The product, BF_3NH_3 , is known as an adduct.

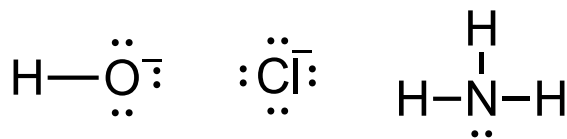
Complex ions

- Complex ions consist of a central metal ion bonded to ligands.
- Central metals ions are Lewis acids and ligands are Lewis bases.
- A coordination bond is formed between the central metal ion and the ligands.
- Example – in the complex ion shown the central metal ion, Cu^{2+} is the Lewis acid.
- The ligands, H_2O molecules, are Lewis bases.

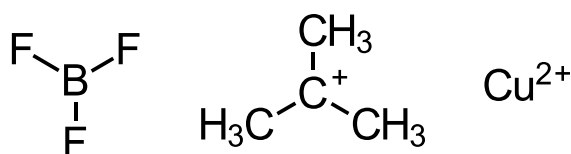


Nucleophiles and electrophiles

- Nucleophiles are electron-rich species that donate an electron pair thereby acting as Lewis bases.
- Examples include the hydroxide ion, the chloride ion and ammonia.



- Electrophiles are electron-deficient species that accept an electron pair, thereby acting as Lewis acids.
- Examples include boron trifluoride, carbocations, and the copper(II) ion.



Exercises:

- 1) Define an acid and base according to the Lewis theory.
- 2) Explain how ammonia (NH₃) is able to act as a Lewis base.
- 3) State the type of bond formed between a Lewis acid and a Lewis base.

Lewis theory vs Bronsted-Lowry theory

- The definitions of acids and bases for each theory are shown in the table below.

Bronsted-Lowry theory	Lewis theory
An acid is a proton donor A base is a proton acceptor	An acid is an electron pair acceptor A base is an electron pair donor

- Bronsted-Lowry theory involves the transfer of protons; if there is no transfer of protons taking place, then the reaction cannot be described using Bronsted-Lowry theory.
- All Bronsted-Lowry acids are also Lewis acids and all Bronsted-Lowry bases are also Lewis bases.
- Not all Lewis acids are Bronsted-Lowry acids (BF_3 , Cu^{2+}).
- The formation of a complex ion can be described using Lewis theory, but not Bronsted-Lowry theory.

Exercise: Explain why the following reaction cannot be described using the Bronsted-Lowry theory of acids and bases.



Reactivity 3.4.8

Understandings:

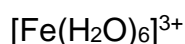
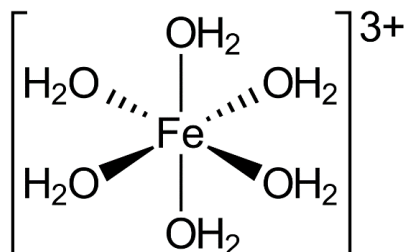
- Coordination bonds are formed when ligands donate an electron pair to transition element cations, forming complex ions.

Learning outcomes:

- Deduce the charge on a complex ion, given the formula of the ion and ligands present.

Complex ions

- A complex ion consists of a central metal ion (usually a transition metal ion) bonded to ligands by coordination bonds.
- The central metal ion acts as a Lewis acid (electron pair acceptor) and the ligands act as Lewis bases (electron pair donors).
- In the example below, the central metal ion is the Fe^{2+} ion and the ligands are water molecules.
- The ligands are bonded to the central metal ion by coordination bonds.

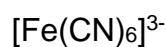
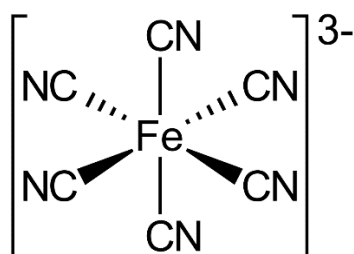


- The coordination number of a complex ion is the number of coordination bonds between the ligands and the central metal ion.
- The above complex ion has a coordination number of six as there are six coordinate covalent bonds between the ligands and the central metal ion.

Exercises:

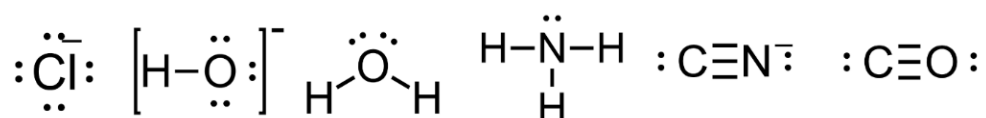
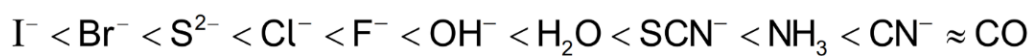
1) Describe the structure of a complex ion.

2) Determine the coordination number and geometry of the following complex ions.



Ligands

- Ligands are species with lone pairs of electrons that form coordination bonds with a central metal ion (they are Lewis bases – electron pair donors).
- Monodentate ligands use only one lone pair of electrons to bond to a central metal ion.



Exercises:

- 1) Outline what is meant by the term ligand.

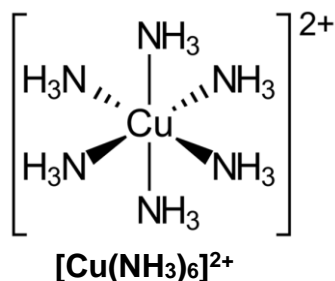
- 2) Explain how ligands are also able to act as Lewis bases.

Deduce the charge on a central metal ion

- The table shows the common ions formed by the transition elements together with their oxidation numbers.

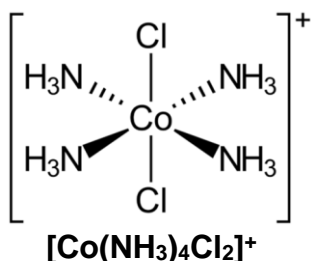
Transition element	Common ions formed	Oxidation number
Chromium	Chromium(II) Cr^{2+}	+2
	Chromium(III) Cr^{3+}	+3
Cobalt	Cobalt(II) Co^{2+}	+2
	Cobalt(III) Co^{3+}	+3
Copper	Copper(I) Cu^+	+1
	Copper(II) Cu^{2+}	+2
Iron	Iron(II) Fe^{2+}	+2
	Iron(III) Fe^{3+}	+3
Nickel	Nickel(II) Ni^{2+}	+2

Example 1:



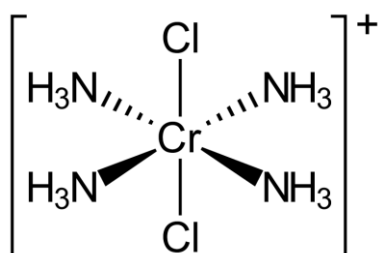
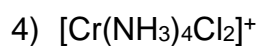
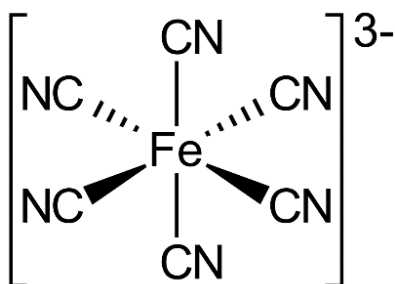
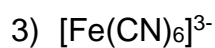
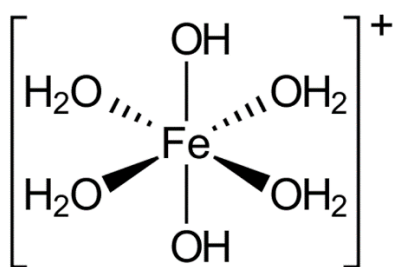
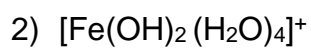
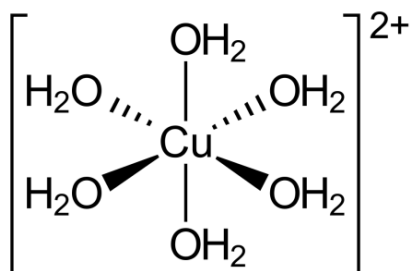
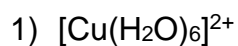
If the ligands are neutral, the charge on the complex ion is the same as the charge on the central metal ion.
The central metal ion is the Cu^{2+} ion (oxidation state +2).

Example 2:



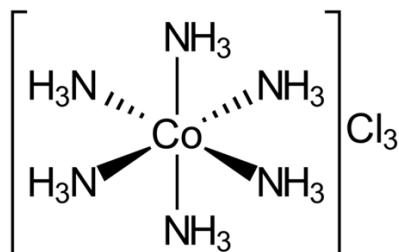
If the ligands are negatively charged, subtract the total charge of the ligands from the charge on the complex ion.
The central metal ion is the Co^{3+} (oxidation state +3).

Exercise: For each of the complex ions, deduce the charge and oxidation state on the central metal ion.



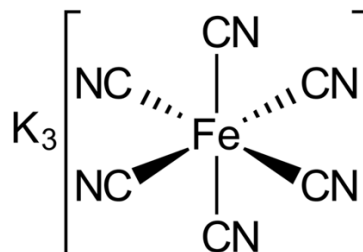
Coordination compounds

- Coordination compounds are composed of a complex ion together with counter ions that cancel out the charge of the complex ion.
- Coordination compounds are neutral (have no overall charge).
- Two examples of coordination compounds are shown below: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$.



$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

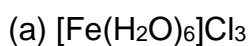
Central metal ion: Co^{3+}
Ligands: six NH_3 molecules
Charge on complex ion: 3+
Counter ions: three Cl^- ions



$\text{K}_3[\text{Fe}(\text{CN})_6]$

Central metal ion: Fe^{3+}
Ligands: six CN^- ions
Charge on complex ion: 3+
Counter ions: three K^+ ions

Exercise: Determine the charge on the complex ion in the following coordination compounds.



Reactivity 3.4.9

Understandings:

- Nucleophilic substitution reactions include the reactions between halogenoalkanes and nucleophiles.

Learning outcomes:

- Describe and explain the mechanisms of the reactions of primary and tertiary halogenoalkanes with nucleophiles.

Additional notes:

- Distinguish between the concerted one-step S_N2 reaction of primary halogenoalkanes and the two-step S_N1 reaction of tertiary halogenoalkanes. Both mechanisms occur for secondary halogenoalkanes.
- The stereospecific nature of S_N2 reactions should be covered.

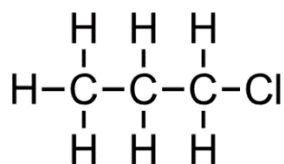
Linking questions:

- Reactivity 2.2 What differences would be expected between the energy profiles for S_N1 and S_N2 reactions?
- Reactivity 2.2 What are the rate equations for these S_N1 and S_N2 reactions?

Nucleophilic substitution reactions

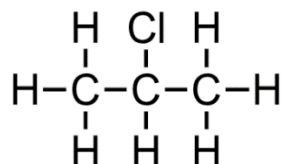
- A nucleophilic substitution reaction (S_N) involves the replacement of an atom, called the leaving group, by a nucleophile.
- Nucleophilic substitution reactions can occur via S_N1 or S_N2 mechanisms.
- S_N1 stands for nucleophilic substitution unimolecular.
- S_N2 stands for nucleophilic substitution bimolecular.
- Primary halogenoalkanes react via the S_N2 mechanism.
- Tertiary halogenoalkanes react via the S_N1 mechanism.
- Secondary halogenoalkanes react via the S_N1 and S_N2 mechanisms.

Primary halogenoalkane



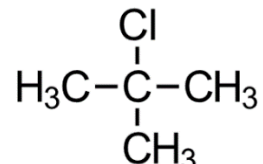
S_N2

Secondary halogenoalkane



S_N1/S_N2

Tertiary halogenoalkane

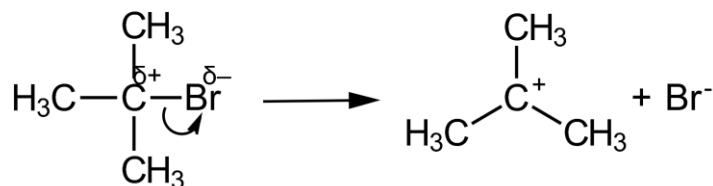


S_N1

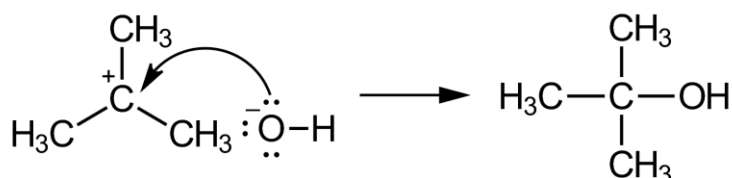
S_N1 mechanism

- The S_N1 mechanism is a two-step mechanism that involves the formation of a carbocation intermediate.
- The first step involves the heterolytic bond fission of the C-X bond.
- In the second step, the nucleophile bonds with the carbocation.

Step one



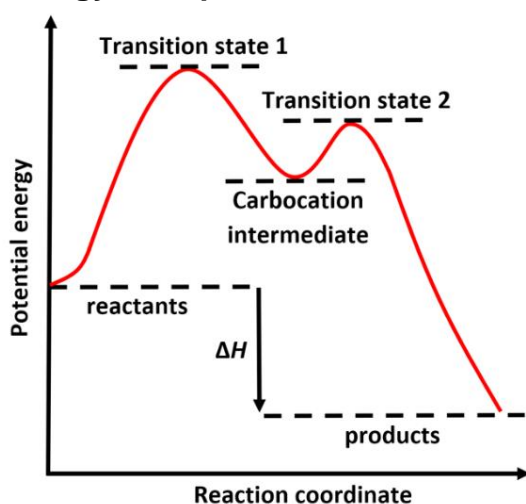
Step two



- The carbocation is stabilised by the electrons from the carbon atoms in the alkyl groups, which is known as the (positive) inductive effect.
- The bulky alkyl groups prevent the nucleophile from attacking on the opposite side to the leaving group, known as steric hindrance.
- S_N1 reactions begin with a single enantiomer and result in the production of a racemic mixture containing equal amounts of two enantiomers. A racemic mixture is known as being optically inactive.
- The S_N1 mechanism is unimolecular; the rate-determining step (the slowest step) depends on the concentration of the halogenoalkane only.
- Example rate expression:



Energy level profile for S_N1 mechanism



Transition state 1

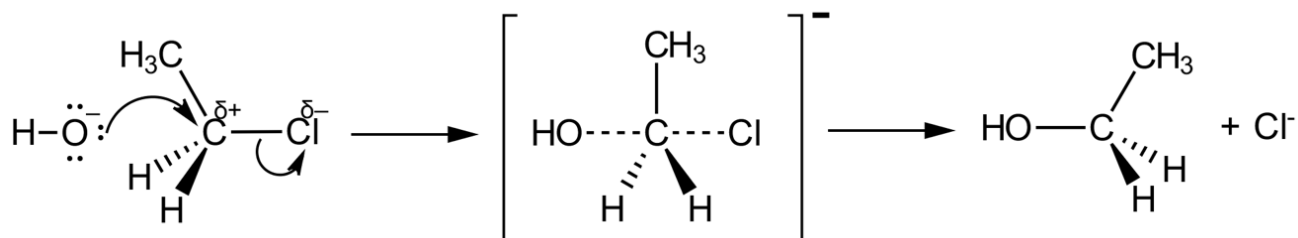
- step with highest potential energy
- formation of carbocation intermediate
- rate-determining step.

Transition state 2

- step with lowest potential energy
- attack by nucleophile on carbocation intermediate.

S_N2 mechanism

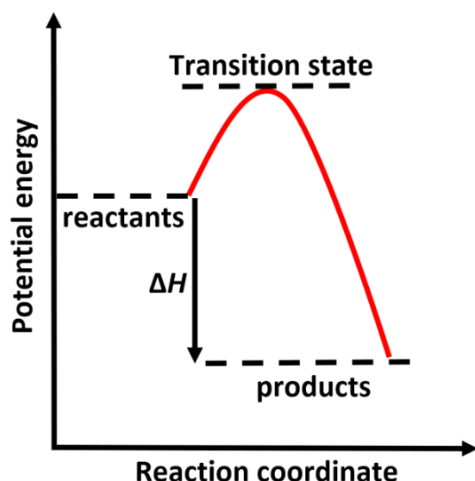
- The S_N2 mechanism is a one-step mechanism that involves the formation of an unstable transition state.
- The nucleophile attacks from the opposite side of the leaving group which is known as a backside attack.
- The C-X bond undergoes heterolytic bond fission.



- In the transition state, the nucleophile and leaving group are both weakly bonded to the carbon atom.
- The backside attack by the nucleophile causes inversion of the atoms around the carbon atom (the S_N2 mechanism is stereospecific).
- The S_N2 mechanism is bimolecular; the rate of reaction depends on both the concentration of the halogenoalkane and the nucleophile.
- Example rate expression:

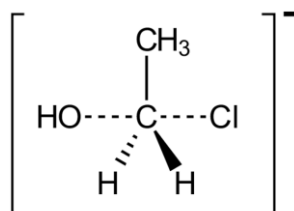
$$\text{rate} = k[\text{halogenoalkane}][\text{nucleophile}]$$
$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}][\text{OH}^-]$$

Energy level profile for S_N2 mechanism



Transition state

- Transition state with both the nucleophile and leaving group weakly bonded to the carbon atom.



Reactivity 3.4.10

Understandings:

- The rate of the substitution reactions is influenced by the identity of the leaving group.

Learning outcomes:

- Predict and explain the relative rates of the substitution reactions for different halogenoalkanes.

Additional notes:

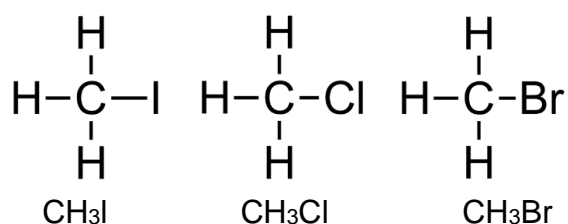
- Different halogenoalkanes should include RCl, RBr and RI.
- The roles of the solvent and the reaction mechanism on the rate will not be assessed.

Linking questions:

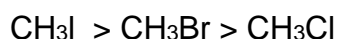
- Structure 3.1 Why is the iodide ion a better leaving group than the chloride ion?

Leaving group and rate of S_N reactions

- The rate of reaction of a nucleophilic substitution reaction depends on the leaving group.
- The strength of the carbon-halogen bond decreases as the radius of the halogen atom increases.
- As the substitution reaction involves breaking this bond, iodoalkanes are the most reactive and fluoroalkanes are the least reactive.
- Example – three halogenoalkanes are shown below, iodomethane, chloromethane and bromomethane.

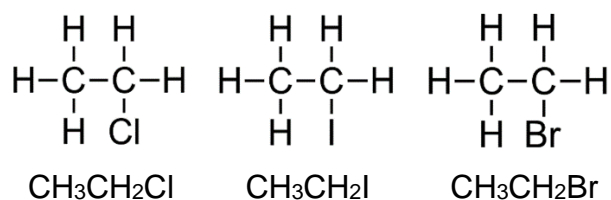


- The fastest rate of reaction would occur with iodomethane because the iodide ion has the largest ionic radius and is the best leaving group.
- The rate of reaction is as follows:



Iodoalkanes (RI) > bromoalkanes (RBr) > chloroalkanes (RCl)

Exercise: Arrange the following halogenoalkanes in order of rate of reaction (fastest first).



Reactivity 3.4.11

Understandings:

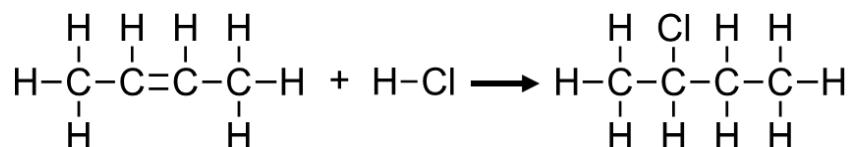
- Alkenes readily undergo electrophilic addition reactions.

Learning outcomes:

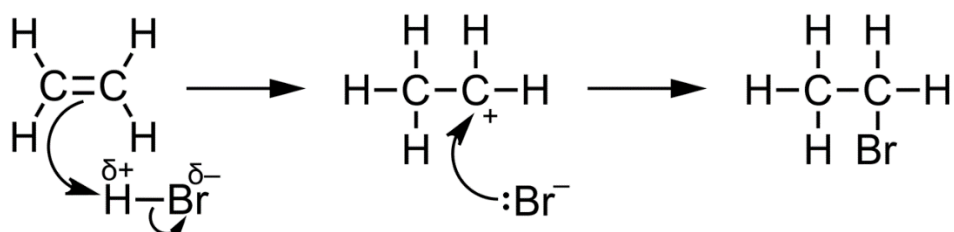
- Describe and explain the mechanisms of the reactions between symmetrical alkenes and halogens, water and hydrogen halides.

Electrophilic addition reactions

- The carbon-to-carbon double bond in an alkene is a region of high electron density.
- This makes the C=C bond attractive to electrophiles.
- When an electrophile reacts with a symmetrical alkene, there is only one possible product.
- Example – when HCl reacts with but-2-ene, only one product, 2-chlorobutane, is produced.

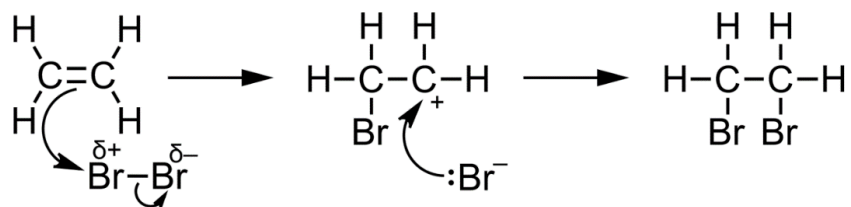


Reaction with HBr



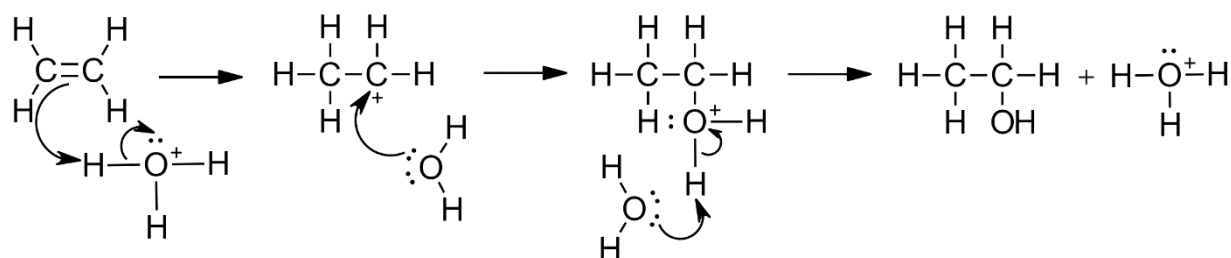
- The H-Br bond undergoes heterolytic fission producing H^+ and Br^- .
- The H^+ bonds with the carbon atom of the C=C bond which results in the formation of a carbocation intermediate.
- The Br^- ion bonds with the carbocation, producing bromoethane.

Reaction with bromine, Br_2



- The Br-Br bond undergoes heterolytic fission producing Br^- and Br^+ .
- The Br^+ ion bonds to one of the carbon atoms of the C=C bond forming a carbocation intermediate.
- The Br^- ion bonds with the carbocation producing 1,2-dibromoethane.

Reaction with water (acid catalysed)



- The O-H bond of the electrophile (H_3O^+) undergoes heterolytic fission.
- The H^+ bonds to the carbon of the $\text{C}=\text{C}$ bond.
- A water molecule bonds with the carbocation forming a protonated ethanol molecule.
- The protonated ethanol molecule loses a proton to form ethanol and a hydronium ion.

Reactivity 3.4.12

Understandings:

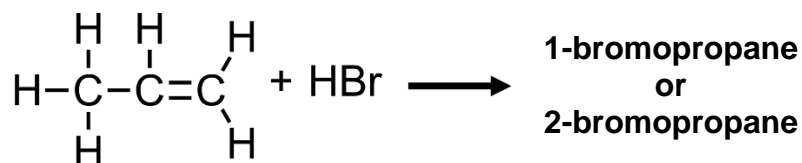
- The relative stability of carbocations in the addition reactions between hydrogen halides and unsymmetrical alkenes can be used to explain the reaction mechanism.

Learning outcomes:

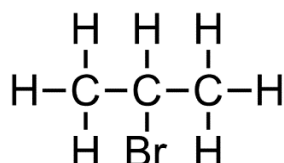
- Predict and explain the major product of a reaction between an unsymmetrical alkene and a hydrogen halide or water.

Markovnikov's rule

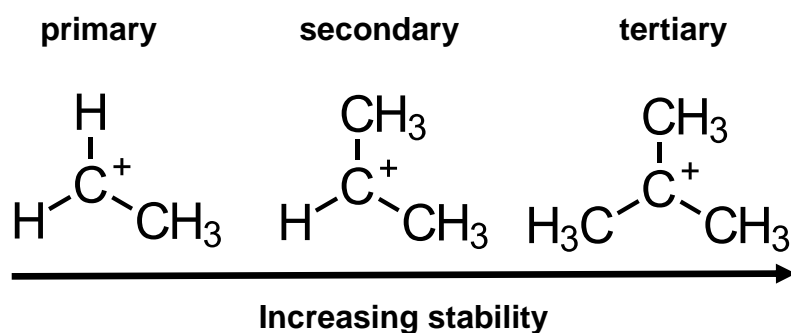
- Markovnikov's rule can be used to predict the major product when a hydrogen halide reacts with an unsymmetrical alkene.
- When an unsymmetrical alkene such as propene reacts with hydrogen bromide, there are two possible products.



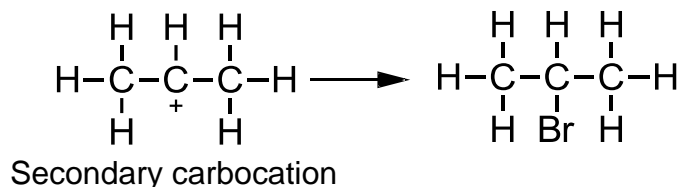
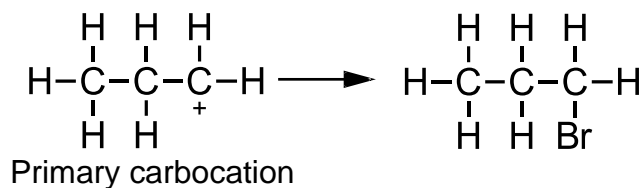
- Markovnikov's rule states that when an unsymmetrical alkene reacts with a hydrogen halide or water, the hydrogen bonds to the carbon that is already bonded to the greatest number of hydrogen atoms.
- The major product of the reaction is 2-bromopropane.



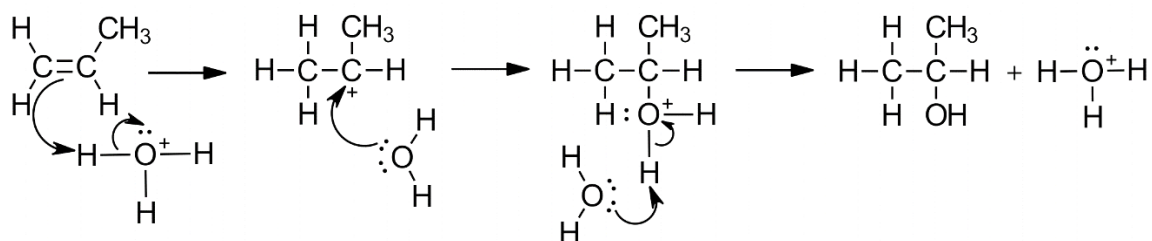
- The product formed depends on the stability of the carbocation.
- Carbocations are stabilised by electron-donating alkyl groups, which is known as the positive inductive effect.
- The more substituted the carbocation (the more alkyl groups bonded to the carbon with the positive charge), the greater the stability.
- The order of stability is: $1^\circ < 2^\circ < 3^\circ$



- When propene reacts with hydrogen bromide, the major product is 2-bromopropane because it involves the formation of a secondary carbocation which is more stable than a primary carbocation.



Reaction of propene with water



- The O-H bond of the electrophile (H_3O^+) undergoes heterolytic fission.
- The H^+ bonds to the carbon of the $\text{C}=\text{C}$ that is bonded to the greatest number of hydrogen atoms.
- A water molecule bonds with the carbocation forming a protonated ethanol molecule.
- The protonated ethanol molecule loses a proton to form ethanol and a hydronium ion.

Reactivity 3.4.13

Understandings:

- Electrophilic substitution reactions include the reactions of benzene with electrophiles.

Learning outcomes:

- Describe and explain the mechanism of the reaction between benzene and a charged electrophile, E^+ .

Additional notes:

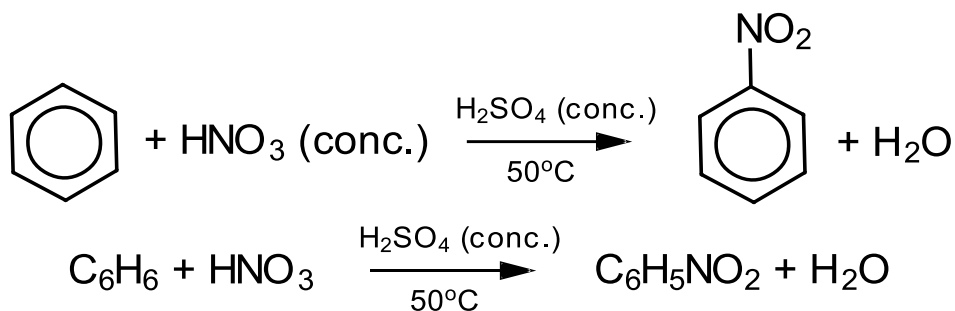
- The formation of the electrophile will not be assessed.

Linking questions:

- Structure 2.2 What are the features of benzene, C_6H_6 , that make it not prone to undergo addition reactions, despite being highly unsaturated?
- Reactivity 3.1 Nitration of benzene uses a mixture of concentrated nitric and sulfuric acids to generate a strong electrophile, NO_2^+ . How can the acid/base behaviour of HNO_3 in this mixture be described?

Nitration of benzene

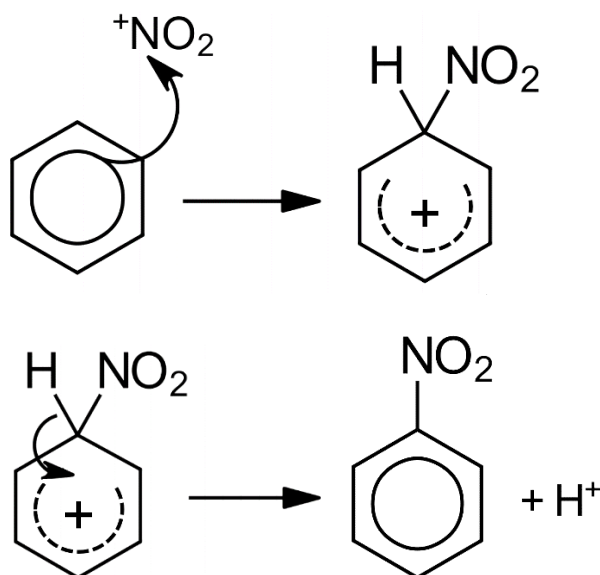
- Benzene reacts with a mixture of concentrated nitric acid (HNO₃) and concentrated sulfuric acid (H₂SO₄) in an electrophilic substitution reaction.
- The products of the reaction are nitrobenzene (C₆H₅NO₂) and water.



- The mixture of concentrated nitric acid and concentrated sulfuric acid is known as a nitrating mixture.
- The sulfuric acid protonates the nitric acid, which then loses a molecule of water to form the nitronium ion, NO₂⁺.



Reaction mechanism



- NO₂⁺ is a strong electrophile and is attracted to the delocalised π electron cloud in the benzene molecule.
- It forms a bond using the π electrons to produce a carbocation intermediate.
- The C–H bond undergoes heterolytic fission with both bonding electrons used to reform the arene ring.
- The H⁺ reacts with the HSO₄⁻ to reform the sulfuric acid catalyst.