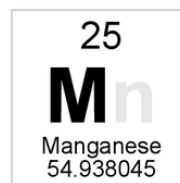
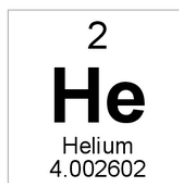
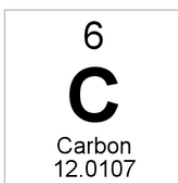
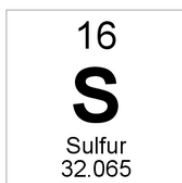
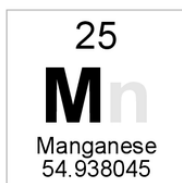


# Reactivity 3.4 HL

# Answers

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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:

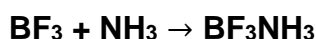
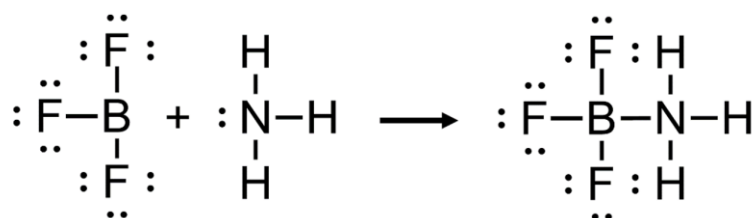
- Apply Lewis acid–base theory to inorganic and organic chemistry to identify the role of the reacting species (3.4.6)
- Draw and interpret Lewis formulas of reactants and products to show coordination bond formation in Lewis acid–base reactions (3.4.7).

#### 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

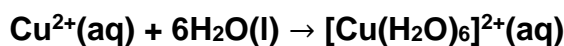
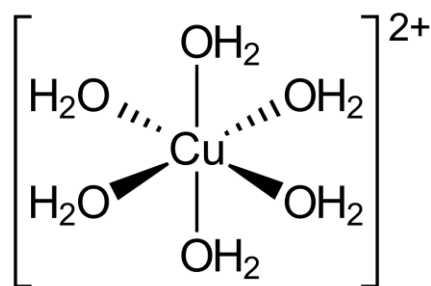
- A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.
- When a Lewis acid and Lewis base react together, the Lewis base donates an electron pair to the Lewis acid.
- A coordination bond is formed between the Lewis acid and the Lewis base.
- Example –  $\text{BF}_3$  and  $\text{NH}_3$  react together to form  $\text{BF}_3\text{NH}_3$ .
- $\text{NH}_3$  acts as a Lewis base by donating an electron pair to  $\text{BF}_3$  which acts as a Lewis acid by accepting the electron pair.



- The product,  $\text{BF}_3\text{NH}_3$ , is known as an adduct.

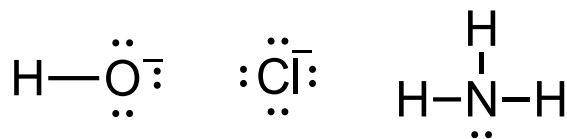
## Complex ions

- 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,  $\text{Cu}^{2+}$  is the Lewis acid.
- The ligands,  $\text{H}_2\text{O}$  molecules, are Lewis bases.

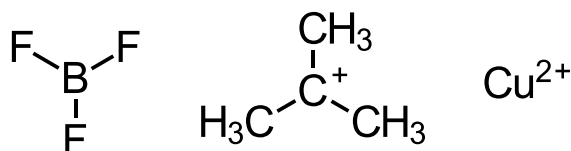


## Nucleophiles and electrophiles

- 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.

A Lewis acid is an electron pair acceptor, a Lewis base is an electron pair donor.

- 2) Explain how ammonia (NH<sub>3</sub>) is able to act as a Lewis base.

Ammonia has a lone pair of electrons that it donates to a Lewis acid.

- 3) State the type of bond formed between a Lewis acid and a Lewis base.

The bond formed is a coordination bond.

## 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 ( $\text{BF}_3$ ,  $\text{Cu}^{2+}$ ).
- 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.



There is no proton transfer in the reaction. The ligands (Lewis bases) use their lone pairs of electrons to form a coordination bond to the central metal ion (Lewis acid).

### Reactivity 3.4.8

#### Understandings:

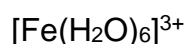
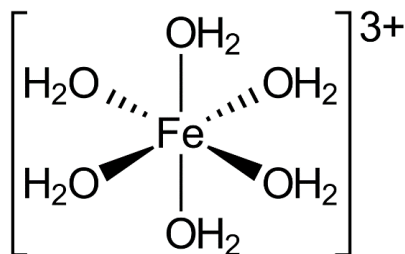
- Coordination bonds are formed when ligands donate an electron pair to transition element cations, forming complex ions.

#### 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  $\text{Fe}^{2+}$  ion and the ligands are water molecules.
- The ligands are bonded to the central metal ion by coordination bonds.



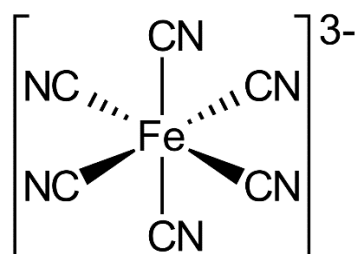
- The coordination number of a complex ion is the number of coordination bonds between the ligands and the central metal ion.
- The above complex ion has a coordination number of six as there are six coordinate covalent bonds between the ligands and the central metal ion.

## Exercises:

- 1) Describe the structure of a complex ion.

A complex ion consists of a central metal ion bonded to ligands by coordination bonds.

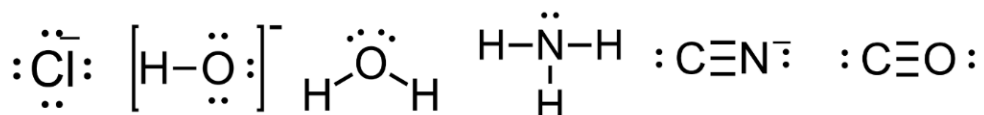
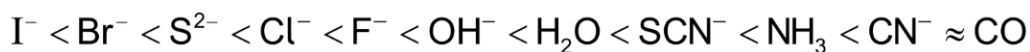
- 2) Determine the coordination number and geometry of the following complex ions.



Coordination number is 6 and geometry is octahedral.

## 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.

A ligand is a species with a lone pair of electrons that forms a coordination bond to a central metal ion. Ligands can be negative ions ( $\text{CN}^-$ ) or neutral molecules ( $\text{NH}_3$ ).

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

Ligands donate electron pairs to the central metal ion, therefore, they act as Lewis bases. The central metal ion is the Lewis acid.

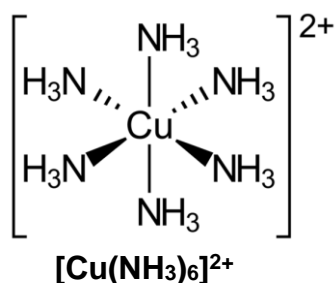


## Deduce the charge on a central metal ion

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

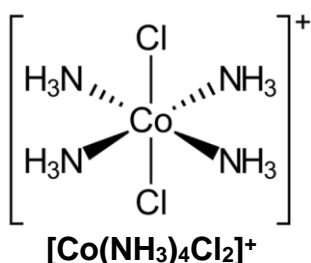
Transition element	Common ions formed	Oxidation number
Chromium	Chromium(II) $\text{Cr}^{2+}$	+2
	Chromium(III) $\text{Cr}^{3+}$	+3
Cobalt	Cobalt(II) $\text{Co}^{2+}$	+2
	Cobalt(III) $\text{Co}^{3+}$	+3
Copper	Copper(I) $\text{Cu}^+$	+1
	Copper(II) $\text{Cu}^{2+}$	+2
Iron	Iron(II) $\text{Fe}^{2+}$	+2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

### Example 1:



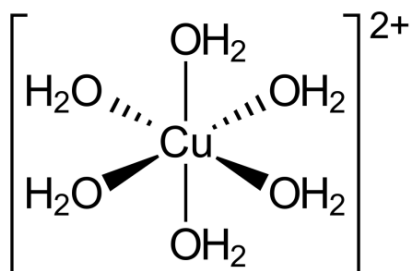
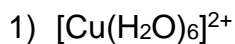
If the ligands are neutral, the charge on the complex ion is the same as the charge on the central metal ion.  
The central metal ion is the  $\text{Cu}^{2+}$  ion (oxidation state +2).

### Example 2:

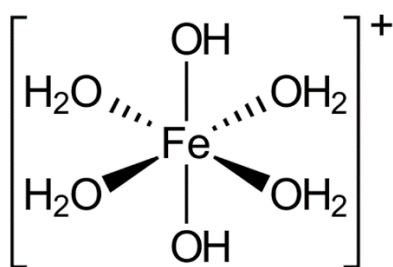
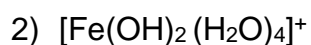


If the ligands are negatively charged, subtract the total charge of the ligands from the charge on the complex ion.  
The central metal ion is the  $\text{Co}^{3+}$  (oxidation state +3).

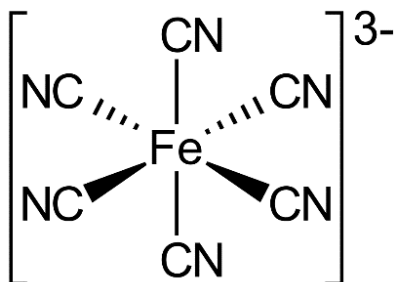
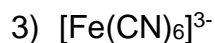
**Exercise:** For each of the complex ions, deduce the charge and oxidation state on the central metal ion.



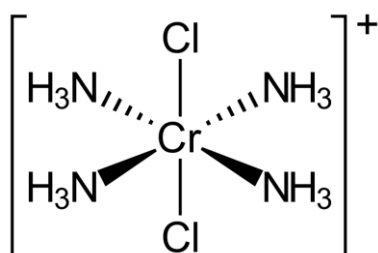
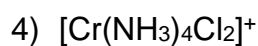
$\text{H}_2\text{O}$  is neutral; the charge on the Cu ion is 2+ ( $\text{Cu}^{2+}$ )  
oxidation state +2



$\text{OH}^-$  has a 1- charge and  $\text{H}_2\text{O}$  is neutral; the charge on the Fe ion is 3+ ( $\text{Fe}^{3+}$ )  
oxidation state +3



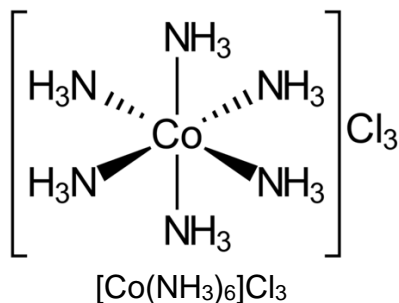
$\text{CN}^-$  has a 1- charge; the charge on the Fe ion is 3+ ( $\text{Fe}^{3+}$ )  
oxidation state +3



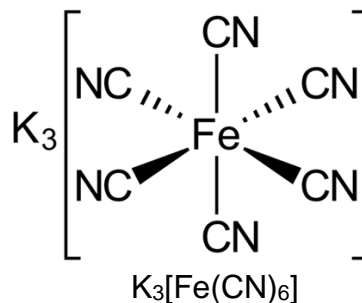
$\text{Cl}^-$  has a 1- charge; the charge on the Fe ion is 3+ ( $\text{Fe}^{3+}$ )  
oxidation state +3

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

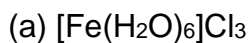


Central metal ion:  $\text{Co}^{3+}$   
Ligands: six  $\text{NH}_3$  molecules  
Charge on complex ion: 3+  
Counter ions: three  $\text{Cl}^-$  ions



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

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



The complex ion is  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

The counter ions are  $3\text{Cl}^-$



The complex ion is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

The counter ions are  $2\text{Cl}^-$

### 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.

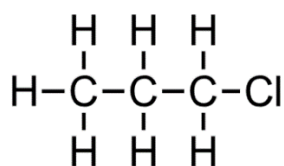
#### Linking questions:

- 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

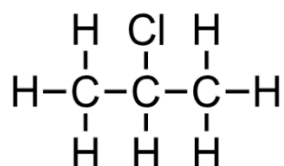
- A nucleophilic substitution reaction ( $S_N$ ) involves the replacement of an atom, called the leaving group, by a nucleophile.
- Nucleophilic substitution reactions can occur via  $S_N1$  or  $S_N2$  mechanisms.
- $S_N1$  stands for nucleophilic substitution unimolecular.
- $S_N2$  stands for nucleophilic 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



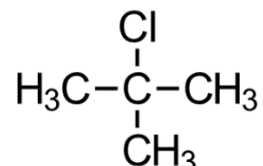
$S_N2$

Secondary halogenoalkane



$S_N1/S_N2$

Tertiary halogenoalkane

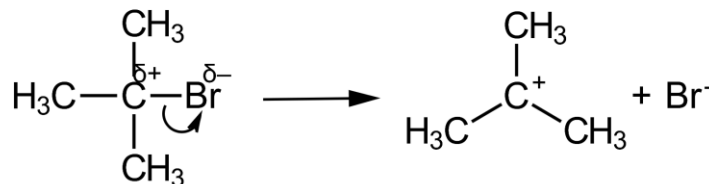


$S_N1$

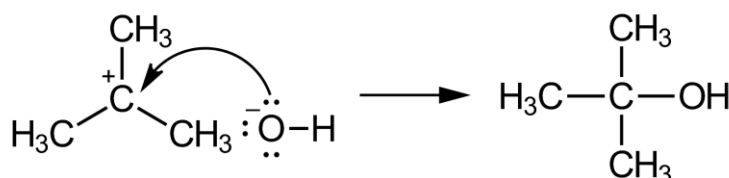
## S<sub>N</sub>1 mechanism

- The S<sub>N</sub>1 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



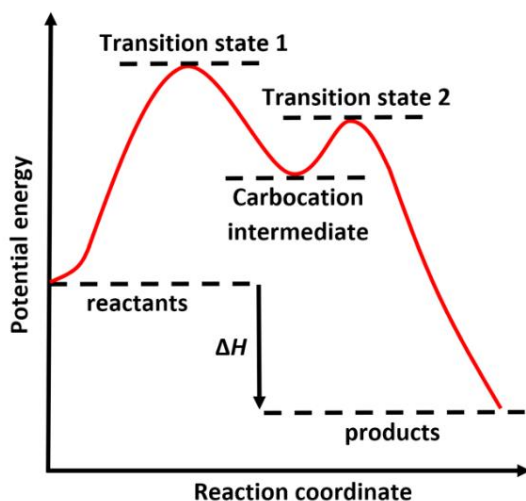
### Step two



- 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<sub>N</sub>1 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<sub>N</sub>1 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<sub>N</sub>1 mechanism



### Transition state 1

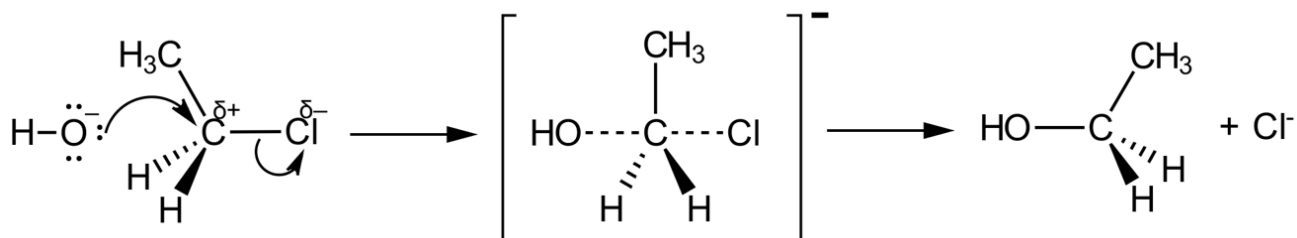
- step with highest potential energy
- formation of carbocation intermediate
- rate-determining step.

### Transition state 2

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

## S<sub>N</sub>2 mechanism

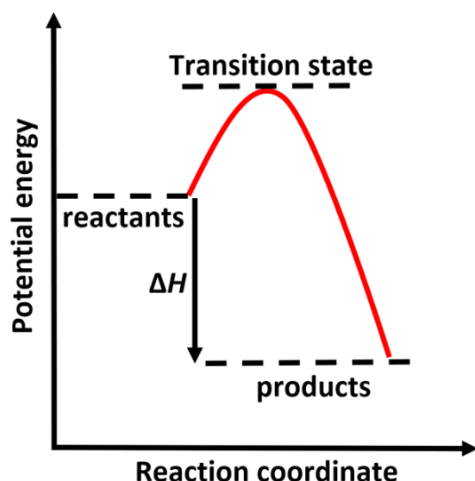
- The S<sub>N</sub>2 mechanism is a one-step mechanism that involves the formation of an unstable transition state.
- The nucleophile attacks from the opposite side of the leaving group which is known as a backside attack.
- The C-X bond undergoes heterolytic bond fission.



- 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<sub>N</sub>2 mechanism is stereospecific).
- The S<sub>N</sub>2 mechanism is bimolecular; the rate of reaction depends on both the concentration of the halogenoalkane and the nucleophile.
- Example rate expression:

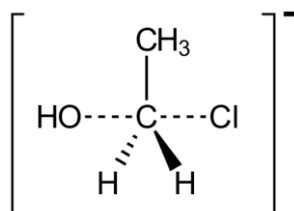
$$\text{rate} = k[\text{halogenoalkane}][\text{nucleophile}]$$
$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}][\text{OH}^-]$$

## Energy level profile for S<sub>N</sub>2 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:

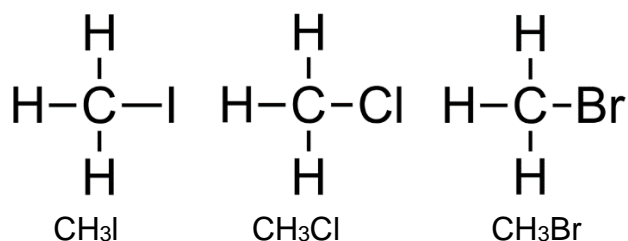
- Different halogenoalkanes should include RCl, RBr and RI.
- The roles of the solvent and the reaction mechanism on the rate will not be assessed.

#### Linking questions:

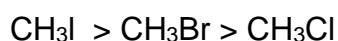
- Structure 3.1 Why is the iodide ion a better leaving group than the chloride ion?

#### Leaving group and rate of S<sub>N</sub> 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.

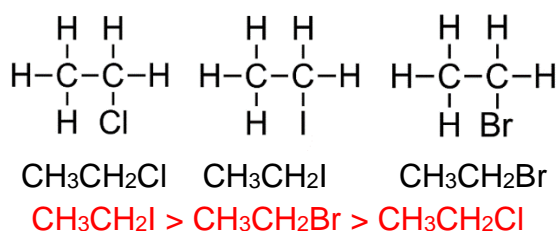


- The fastest rate of reaction would occur with iodomethane because the iodide ion has the largest ionic radius and is the best leaving group.
- The rate of reaction is as follows:



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

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





### **Reactivity 3.4.11**

#### **Understandings:**

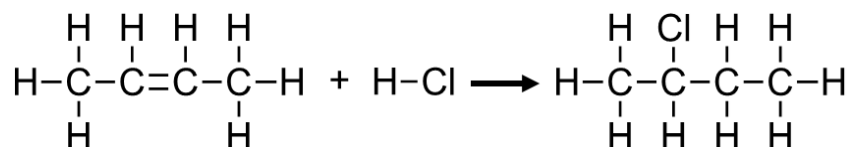
- Alkenes readily undergo electrophilic addition reactions.

#### **Learning outcomes:**

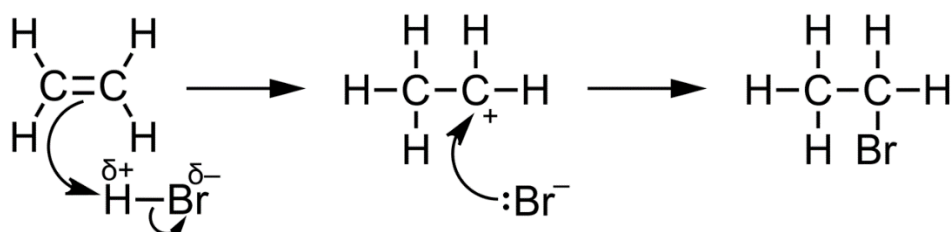
- Describe and explain the mechanisms of the reactions between symmetrical alkenes and halogens, water and hydrogen halides.

## 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.

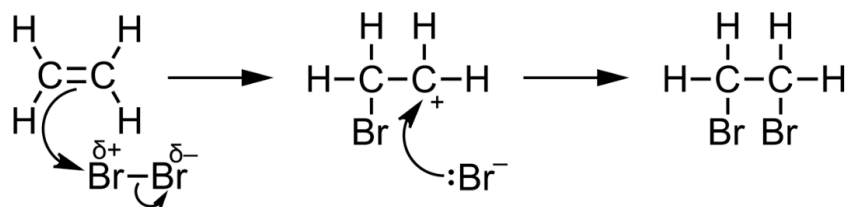


### Reaction with HBr



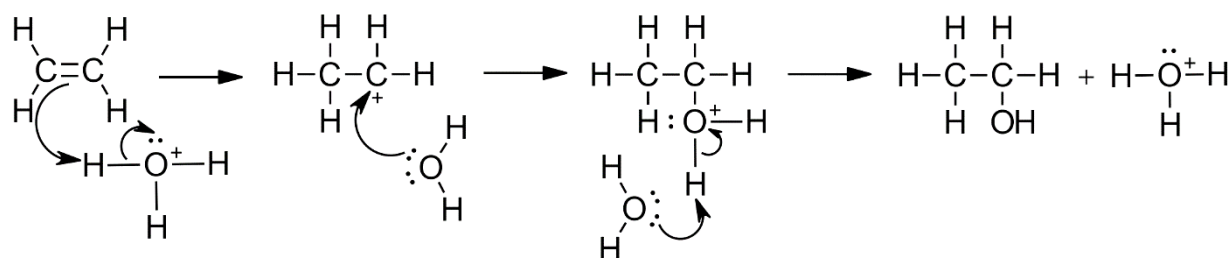
- The H-Br bond undergoes heterolytic fission producing  $\text{H}^+$  and  $\text{Br}^-$ .
- The  $\text{H}^+$  bonds with the carbon atom of the C=C bond which results in the formation of a carbocation intermediate.
- The  $\text{Br}^-$  ion bonds with the carbocation, producing bromoethane.

### Reaction with bromine, $\text{Br}_2$



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

### Reaction with water (acid catalysed)



- The O-H bond of the electrophile ( $\text{H}_3\text{O}^+$ ) undergoes heterolytic fission.
- The  $\text{H}^+$  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:**

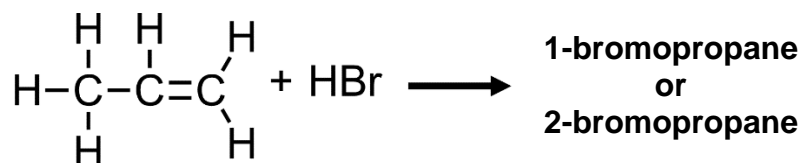
- The relative stability of carbocations in the addition reactions between hydrogen halides and unsymmetrical alkenes can be used to explain the reaction mechanism.

#### **Learning outcomes:**

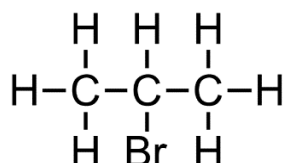
- Predict and explain the major product of a reaction between an unsymmetrical alkene and a hydrogen halide or water.

## Markovnikov's rule

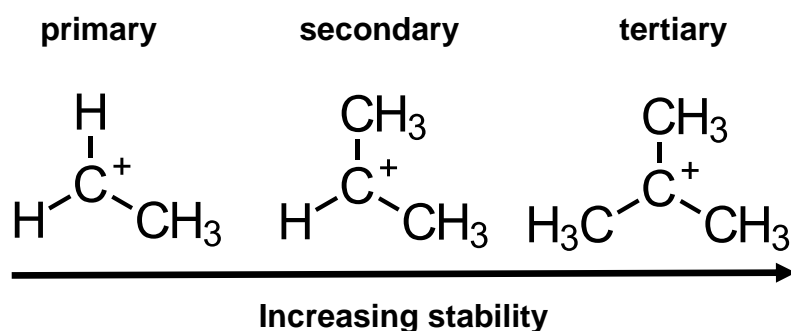
- Markovnikov's rule can be used to predict the major product when a hydrogen halide reacts with an unsymmetrical alkene.
- When an unsymmetrical alkene such as propene reacts with hydrogen bromide, there are two possible products.



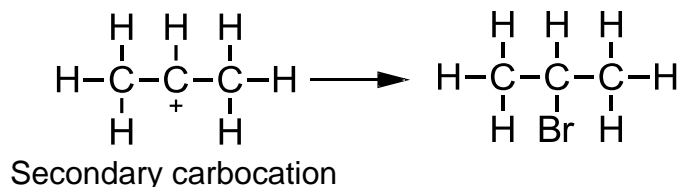
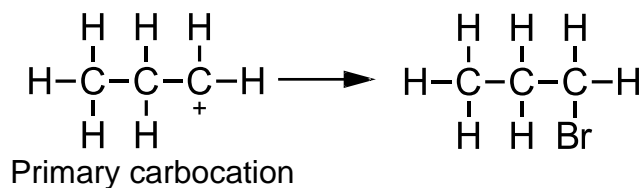
- Markovnikov's rule states that when an unsymmetrical alkene reacts with a hydrogen halide or water, the hydrogen bonds to the carbon that is already bonded to the greatest number of hydrogen atoms.
- The major product of the reaction is 2-bromopropane.



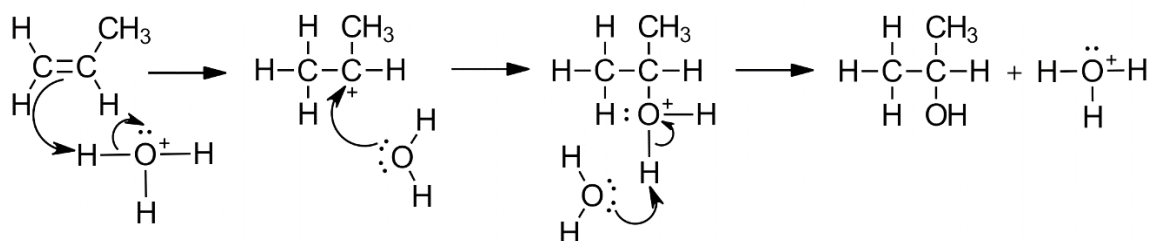
- The product formed depends on the stability of the carbocation.
- Carbocations are stabilised by electron-donating alkyl groups, which is known as the positive inductive effect.
- The more substituted the carbocation (the more alkyl groups bonded to the carbon with the positive charge), the greater 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 ( $\text{H}_3\text{O}^+$ ) undergoes heterolytic fission.
- The  $\text{H}^+$  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.

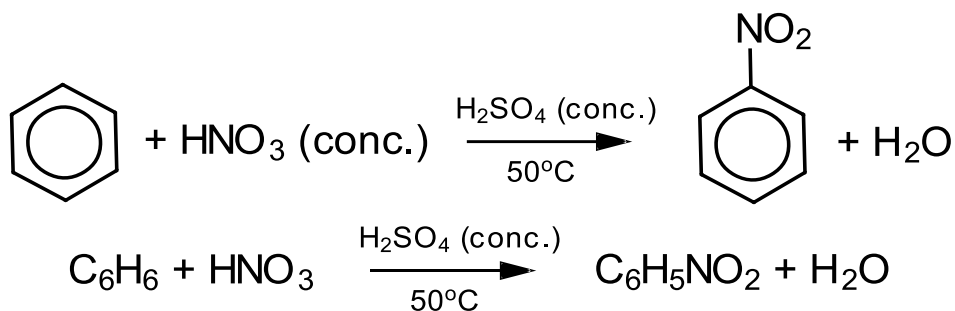
#### Linking questions:

- 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

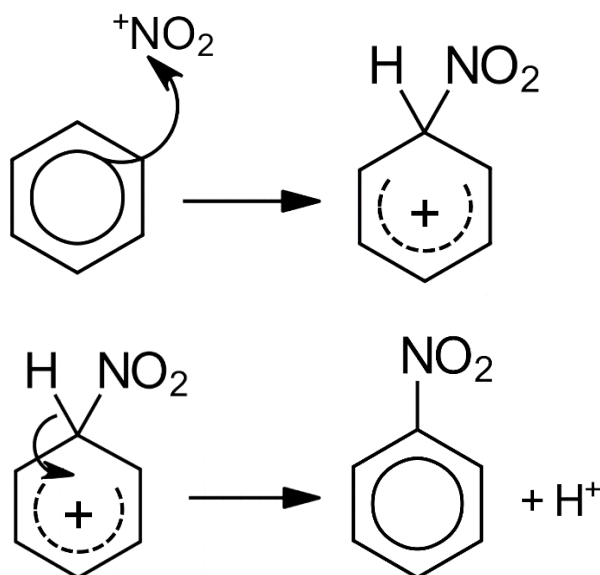
- Benzene reacts with a mixture of concentrated nitric acid (HNO<sub>3</sub>) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in an electrophilic substitution reaction.
- The products of the reaction are nitrobenzene (C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>) and water.



- 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, NO<sub>2</sub><sup>+</sup>.



## Reaction mechanism



- NO<sub>2</sub><sup>+</sup> 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<sup>+</sup> reacts with the HSO<sub>4</sub><sup>-</sup> to reform the sulfuric acid catalyst.