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GENERAL CHEMISTRY B

STUDY GUIDE FOR
CHE1502

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SOUTH AFRICA

PRETORIA

CONTENTS

INTRODUCTION

Welcome to the General Chemistry B Module. Now that you have completed the module General Chemistry A, you will be able to apply the basic principles that you have learnt to two new exciting sub-disciplines of chemistry – physical chemistry and organic chemistry.

This module is divided into two parts:

Part 1: Introductory Physical Chemistry
Part 2: Introductory Organic Chemistry

Part 1

Introductory Physical Chemistry

Physical chemistry is a branch of chemistry which investigates the effects of chemical structure on physical properties of matter. It aims to develop a fundamental understanding at the molecular and atomic level of how materials behave and how chemical reactions occur; knowledge that is relevant in nearly every area of chemistry. It also provides the basis for modern methods of measurements within all areas of Chemistry.

STUDY UNIT 1

Gases

1.1 Introduction

Gases are everywhere! We breathe them, we rely on them for our weather, we use them to float ships on the ocean. There are very few activities that you could think of that do not involve gases in some way or another. It makes sense that we need to understand their behaviour.

Gases behave very differently to liquids and solids. A gas will always occupy the whole of its container, irrespective of its quantity. Fortunately for us, gases are the most easily understood form of matter, and different gases behave quite similarly as far as their physical properties are concerned.

By the end of this chapter, you will be able to explain the physical properties and behaviour of ideal gases.

1.2 Outcomes

After studying this study unit you should be able to:

- Describe the concept of pressure.
- Give the different units in which pressure is measured and convert various units.
- Explain the concept of absolute temperature and convert °Celsius to Kelvin.
- Use the correct units of volume and amount of a gas.
- Explain Boyle’s law.
- Explain Charles’ law.
- Explain Avogadro’s law.
- Do calculations based on Boyle’s, Charles’ and Avogadro’s laws.
- Explain the Ideal-Gas Equation.
- Describe an ideal gas.
- Explain how the value and units of R relate to the units of P, V, n and T.
- Define Standard Temperature and Pressure.
- Relate the Ideal-Gas Equation to the gas laws.
- Do calculations based on all of the above.
- Calculate the density of a gas.
- Explain Dalton’s law of partial pressures.
- Calculate partial pressures of gases.
- Calculate the mole fraction of gases in a mixture.
- Calculate the total pressure of a mixture of gases.

1.3 Fundamental properties of gases

1.3.1 Pressure

When gas molecules collide with the walls of a container, they exert a force on it. This force is known as pressure, and is defined as force per unit area (Newton/meter^2). The standard unit of pressure is the Pascal (Pa), where 1 Pa = 1 N/m^2. However, units such as Torr, millimetres of mercury (mm Hg) and atmosphere (atm) are also frequently used, and it is vital that you know how to convert these units from one to the other.

$$1 \text{ atm} = 760 \text{ Torr} = 760 \text{ mm Hg} = 101.325 \text{ kPa} = 101325 \text{ N/m}^2 = 101325 \text{ Pa}$$

When doing calculations, it is important that you remember to use the same pressure units throughout the entire calculation. These units must also be compatible with the units of the other quantities which appear in the calculation.

1.3.2 Temperature

As with pressure, a change in temperature will also affect the behaviour of a gas. When doing calculations involving gases, the absolute temperature scale, known as the Kelvin scale is used. You should *always* use temperature in Kelvin for gas calculations. The unit for Kelvin is K, where 0 K = -273.15 °C. Converting from °Celsius to Kelvin is easy, and is done using the following formula:

$$T\ (\text{K}) = T\ (^\circ\text{C}) + 273.15$$

1.3.3 Volume and amount

The behaviour of any given quantity of gas depends not only on pressure and temperature, but also on the volume of the gas and on the amount of gas involved. A gas will always expand to fill its container, so the volume of a gas is equal to the volume of the container in which it is held. The unit for volume is litres (L) or cubic decimetres (dm^3). The amount of gas is denoted by the letter n, where n = number of moles of the gas. If you are given a quantity of a gas in grams (g), you should *always* convert this to number of moles before proceeding with the calculation.

Activity 1.1

Perform the following pressure and temperature conversions and report the answers using the correct units:

(i) 0.90 atm to Torr

(ii) 16.314 °C to Kelvin

(iii) 1.37 atm to Pascals

1.4 The gas laws

The equations that express the relationships between temperature (T), pressure (P), volume (V) and number of moles of gas (n) are known as *gas laws*.

1.4.1 Boyle's law: The pressure-volume relationship

At a constant temperature, the pressure of a gas is inversely proportional to the volume. This means that as the pressure gets smaller, the volume of the gas increases. For example, as a helium-filled balloon rises into the atmosphere, the atmospheric pressure becomes less and less, and the volume of the balloon gets larger and larger until the balloon finally bursts. This relationship between pressure and volume is known as Boyle's law.

Boyle's law: At constant temperature, the volume of a fixed amount of gas is inversely proportional to its pressure. (Note that "proportional" is expressed by the symbol "α"). Mathematically, this is written as:

$$\mathrm{P}\ \alpha\ \frac{1}{V}$$

OR $$\mathrm{P} = \text{constant} \times \frac{1}{V}$$

OR $PV = \text{constant}$

Let’s see how Boyle’s law can be used in practice: Consider a given amount of gas at a given temperature. Suppose that the initial volume of the gas is V_1 and the initial pressure is P_1. From Boyle’s law:

$$P_1V_1 = \text{constant}$$

If we change the volume of the gas to V_2, so that the pressure becomes P_2, Boyle’s law tells us that:

$$P_2V_2 = \text{constant}$$

Combining these two equations gives:

$$P_1V_1 = P_2V_2$$

This equation is a workable form of Boyle’s law which we can use when the temperature and amount of gas are kept constant.

Sample Exercise 1.1

A balloon which is filled with helium gas to an initial volume of 0.8 L has a pressure of 150 kPa. The balloon rises into the atmosphere, and it bursts at a volume of 1.5 L. What will the gas pressure be when it bursts?

Solution

From Boyle’s law, $P_1V_1 = P_2V_2$. This rearranges to:

$$P_2 = \frac{P_1V_1}{V_2} = \frac{150\text{ kPa} \times 0.8\text{ L}}{1.5\text{ L}} = 80\text{ kPa}$$

The balloon will burst at a gas pressure of 80 kPa.

1.4.2 Charles' law: The temperature-volume relationship

At a constant pressure, the volume of a gas is proportional to its temperature. As the temperature of a gas increases, so will its volume. A balloon will expand when we heat it and shrink when we put it in the fridge. This relationship between pressure and volume is known as Charles' law.

Charles' law: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature.

Mathematically, this is written as:

$$V \alpha T \qquad \textbf{OR} \qquad \frac{V}{T} = \text{constant}$$

As with Boyle's law, we can formulate a workable form of Charles' law which relates

an initial set of conditions (denoted by subscript $_1$) and final set of conditions (denoted by subscript $_2$). From Charles' law:

$$\frac{V_1}{T_1} = \text{constant}$$

If we change the temperature of the gas to T_2, so that the volume becomes V_2, Charles' law tells us that:

$$\frac{V_2}{T_2} = \text{constant}$$

Combining these two equations gives: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

1.4.3 Avogadro's law: The amount-volume relationship

Avogadro found that at a fixed temperature and pressure, the more molecules a gas contains, the greater its volume will be. This makes sense, because more molecules should take up more space. Avogadro hypothesised that equal volumes of all gases at the same temperature and pressure should contain the same number of molecules or moles of gas. From this hypothesis, he formulated the relationship between amount of gas and volume, a relationship known as Avogadro's law.

Avogadro's law: At constant temperature and pressure, the volume of gas is directly proportional to the number of moles of gas.

Mathematically, this is written as:

$$n \alpha V \quad \textbf{OR} \qquad V = \text{constant} \times n$$

Activity 1.2

If you have a gas cylinder which has a fixed volume filled with argon, what will happen to the gas pressure if you do the following?

(i) *Let half of the gas molecules out of the cylinder while keeping the temperature constant?*
(ii) *Increase the temperature by 25%?*
(iii) *Transfer all the gas to another cylinder of double the size, at the same temperature?*

1.5 The ideal gas equation

1.5.1 Combining the gas laws

Each of the gas laws describes the relationship between two of the four variables, P, V, n and T, while the other two variables are kept constant. These gas laws can be combined into a more general gas law:

$V \alpha \frac{nT}{P}$, or, if we add a proportionality constant, R, we obtain:

$$V = R(\frac{nT}{P})$$

which we can rewrite in the more common form:

$$PV = nRT$$

This equation is called the Ideal-gas equation, because it defines the state of any ideal gas.

1.5.2 Ideal gases

An *ideal gas* is a gas whose behaviour is completely described by the ideal-gas equation. Such gases are hypothetical gases and do not really exist in nature. In nature, attractive forces between molecules cause the gas to deviate from ideal behaviour, and these gases are appropriately called *real gases*. There are separate equations to calculate the state of real gases, but they are quite complicated, and involve complex mathematics. Fortunately for us, if the pressure is not extremely high, and if the temperature is not extremely low, many gases approximate the behaviour of ideal gases and using the ideal-gas equation will give us values of P, V, n and T which are close to the true values. For purposes of this module, you may apply the ideal-gas equation for calculations involving gases, but you should still be aware of the existence of real gases, and you will learn how to solve real-gas problems at a later stage in your chemistry studies.

1.5.3 The gas constant, R

In the ideal-gas equation, the term R is called the *universal gas constant*, or simply the *gas constant*.

$$R = 0.08206\ \text{L.atm.mol}^{-1}\cdot\text{K}^{-1}$$

The constant, R, often causes confusion because it can be expressed in different ways.

The way R is expressed depends on the units of P, V, T and n.

If we want to measure a six-foot man, and want to express the units in feet, he is six feet tall (Height = 6 ft). If we were working in centimetres, then he is 183 centimetres tall (Height = 183 cm). It is still the same height, but the numerical value and units in which we express his height depend on the units in which we are measuring.

Similarly, if we are working with pressure in <u>atm</u>, volume in L, amount in mol, and temperature on K, then R is expressed as $R = 0.08206\ \text{L.atm.mol}^{-1}\cdot\text{K}^{-1}$.

However, if we are working with pressure in <u>kPa</u>, volume in L, amount in mol, and temperature on K, then R is expressed as $R = 8.314\ \text{L.kPa.mol}^{-1}\cdot\text{K}^{-1}$.

It is still the same constant, just expressed differently! We can verify that it is the same constant, because 1 atm = 101.325 kPa, so if we multiply and cancel out our units, we get:

$$(0.08206\,\frac{L.\cancel{atm}}{K.mol}) \times (101.325\,\frac{kPa}{\cancel{atm}}) \;=\; 8.314\,\frac{L.kPa}{K.mol}$$

1.5.4 STP (Standard temperature and pressure)

If experiments are always conducted under the same conditions, it allows comparisons to be made between different sets of data. Standard Temperature and Pressure (STP) is a standard set of conditions which has been defined for such experimental measurements.

The standard conditions corresponding to STP are:
Pressure = 1 bar = 100 000 Pa = 100 kPa
Temperature = 0°C = 273.15 K

1.5.5 Relating the ideal-gas equation and the gas laws

Using the Ideal-Gas equation, it becomes easy to derive any relationship between any of the variables, P, V, n and T. For example:

If PV = nRT, and n and T are constant, then PV is constant, and we have Boyle's law! (Remember that R is also constant)
If PV = nRT then $\frac{V}{T} = \frac{nR}{P}$. If P and n are constant, then $\frac{V}{T}$ is constant and we have Charles' law!

In general, if we have any two sets of conditions, then:

$$P_1V_1 = n_1RT_1 \quad \text{and} \quad P_2V_2 = n_2RT_2$$

By manipulating these two equations, we can also write them as:

$$\frac{P_1V_1}{n_1T_1} = R \quad \text{and} \quad \frac{P_2V_2}{n_2T_2} = R.$$

But since R is constant, this becomes: $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$.

Sample Exercise 1.2

For two sets of conditions, derive the relationship between the initial and final pressure and number of moles, when the volume and temperature are kept constant.

Solution

If we have two sets of conditions, with constant volume and temperature, then:
$P_1V=n_1RT$ and $P_2V=n_2RT$.

$$\text{so: } \frac{P_1}{n_1} = \frac{RT}{V} \quad \text{and} \quad \frac{P_2}{n_2} = \frac{RT}{V}.$$

But since $\frac{RT}{V}$ is constant, the relationship becomes: $\frac{P_1}{n_1} = \frac{P_2}{n_2}$.

Activity 1.3

Determine the number of moles in a sample of gas for each of the following sets of conditions:

(i) At a volume of 3.0 L, a temperature of 32 °C and a pressure of 0.962 atm.
(ii) At STP.

1.6 Gas densities and molar mass

The density (ρ) of a material is defined as its mass (m) divided by its volume (V).

$$\rho = \frac{\mathrm{m}}{\mathrm{V}}$$

We can rearrange the Ideal-Gas equation to derive a convenient new equation for the density of a gas as follows:

$$\frac{n}{V} = \frac{P}{RT}$$

If we multiply both sides by the molar mass, M, then:

$$\frac{nM}{V} = \frac{PM}{RT}$$

For the mass of a substance, we have m = nM. If we multiply $\frac{n}{V}$ by M, we find that $\frac{nM}{V}$ equals the density (*ρ)*, with units, $g.L^{-1}$. We can derive this from the units for n, M, m and V.:

$$\frac{mol}{L} \times \frac{g}{mol} = \frac{g}{L}$$ which correspond to the variables:

$$\frac{n}{V} \times \mathrm{M} = \rho$$

Therefore, the density of a gas is given by the equation:

$$\rho = \frac{PM}{RT}$$

Activity 1.4

A drop of liquid nitrogen, $N_{2\,(l)}$, has a density of 0.808 $g.mL^{-1}$. Assume the drop has a volume of 0.030 mL, what volume of gas will be produced when the drop is heated to 15°C at a pressure of 0.97 atm?

1.7 Gas mixtures and partial pressures

1.7.1 Dalton's law of partial pressures

Since gas molecules are very far apart, we can assume that they behave independently. John Dalton observed that if you have more than one gas mixed together in a container, you can calculate the total pressure in the container by calculating the pressure of each gas alone, and then adding these pressures together. The pressure exerted by a single component of the gas mixture is called the **partial pressure** of that component.

Dalton's law of partial pressures: In a gas mixture, the total pressure is given by the sum of the partial pressures of each component.

Mathematically, this is written as:

$$P_t = P_1 + P_2 + P_3 + ...$$

or, since $P_1 = n_1(\frac{RT}{V})$, $P_2 = n_2(\frac{RT}{V})$ and $P_3 = n_3(\frac{RT}{V})$, we can also write this as:

$$P_t = (n_1 + n_2 + n_3 + ...)\ (\frac{RT}{V}),$$ or simply:

$$P_t = n_t\,\frac{RT}{V}$$

where n_t is the total number of moles of the mixture.

1.7.2 Partial pressures and mole fractions

The mole fraction of a gas (gas 1) in a mixture of gases is defined as:

$$X_1 = \frac{n_1}{n_t}$$

where n_1 is the number of moles of gas 1 and n_t is the total number of moles of all the gases in the mixture.

The mole fraction is a dimensionless number without units, because it tells you what fraction an amount of a particular gas occupies in a mixture of gases.

The partial pressure of a gas can be related to the total pressure by the equation:

$$P_1 = X_1P_t$$

Activity 1.5

A mixture of 1.45 g nitrogen gas (N_2) and 2.10 g argon gas (Ar) is placed in a 2.50 L container at 35.5 °C.

Calculate:

(i) The partial pressure of each gas.

(ii) The mole fraction of each gas.

(iii) The total pressure.

Summary

You should now be able to process and evaluate the gaseous state and the gas laws.

More specifically, you should be able to:

- Evaluate fundamental properties of all gases, namely, pressure, volume, temperature, and amount.
- Analyze properties of gases using gas laws.
- Define standard temperature and pressure.
- Evaluate the relationship between mole, mass, volume and density of gases.
- Explain and apply gas mixtures and partial pressures.

STUDY UNIT 2

Thermochemistry

2.1 Introduction

We all depend on heat for our existence. The sun heats the earth making it suitable for life. We need heat to cook our food. When we accidentally touch the stove while cooking food, we are reminded just how much energy is contained in that stove plate.

In this study unit, you will learn all about heat. You will be introduced to the thermodynamic quantity called enthalpy, and Hess's law, which will allow you to calculate changes in enthalpy. You will examine calorimetry, which we use to measure heat changes in chemical processes.

Have you ever wondered which is the best way to cool a hot cup of tea down to drinking temperature? Should you add the milk immediately, and then let the tea cool down, or should you let your tea cool down first, and then add the milk just before drinking it? Which way will it cool the fastest? By the end of this chapter, you should be able to answer this question.

2.2 Outcomes

After studying this study unit you should be able to:

- Describe endothermic and exothermic processes.
- Explain what is meant by a state function.
- Explain enthalpy as a measure of heat lost or gained at constant pressure.
- Define the 'standard state' at which enthalpies are tabulated, and explain the difference between ΔH and $\Delta H°$.
- Interpret thermochemical equations.
- Explain calorimetry.
- Define heat capacity, molar heat capacity and specific heat capacity.
- Do heat capacity calculations.
- Explain constant-pressure calorimetry.
- Explain Hess's law.
- Use Hess's law to calculate enthalpy changes in chemical reactions.

2.3 Endothermic and exothermic processes

A process in which a system absorbs heat from its surroundings is called **endothermic.** A process in which a system gives off heat to its surroundings is called **exothermic.**

Usually, in the laboratory, you can tell the difference between these two reactions by feeling the container in which the reaction is taking place. An endothermic reaction feels cold, whereas an exothermic reaction feels hot.

Forward knowledge:

(Refer to the section called "Enthalpy" for an explanation of ΔH.)

An endothermic process has a positive ΔH value.

An exothermic process has a negative ΔH value.

2.4 Enthalpy

2.4.1 What is enthalpy?

During a chemical reaction, heat may be absorbed or given off to its surroundings. This heat flow is measured quite easily in the laboratory. If we perform an experiment in a container which is open to the surroundings, the pressure at which the experiment takes place is at constant pressure.

Before you go any further, make 100% sure that you understand the following important concepts, or the rest of this chapter will make no sense at all. If you struggle with any of these, revisit the relevant section in your textbook:

- Make sure you understand the difference between heat and temperature.
- You should fully understand the concept of a state function.
- You need to understand what constitutes ‘the system’ and what constitutes ‘the surroundings.’
- Do you understand why a chemical reaction carried out in an open container always occurs at constant pressure? What is that pressure?

Now that you have mastered these concepts, it’s time for an explanation of what enthalpy means:
The heat transferred between the system and surroundings during a chemical reaction carried out *at constant pressure* is called **enthalpy, H**. However, in a laboratory, we can only measure the *change* in enthalpy, so a new explanation is needed:

The **change in enthalpy, ΔH**, equals the heat gained or lost at constant pressure.

Heat transferred *from surroundings* to the system is a positive change in enthalpy, i.e. $\Delta H > 0$ for an endothermic reaction. Conversely, heat transferred *from a system* to the surroundings is a negative change in enthalpy, i.e. $\Delta H < 0$ for an exothermic reaction.

2.4.2 Enthalpy of reaction

For a reaction:

$$\text{reactants} \rightarrow \text{products}$$

the change in enthalpy is equal to the difference between the final enthalpy (the enthalpy of the products) minus the initial enthalpy (the enthalpy of the reactants.)

Mathematically, we write this as:

$$\Delta H = H_{products} - H_{reactants}$$

Since ΔH is the enthalpy change for this reaction, it is often called the **enthalpy of reaction** or simply the **heat of reaction**, and is then written as ΔH_{rxn}. From this equation, we can see that ΔH depends only on the initial and final states of the system, and not on how the change occurred. ΔH is therefore a **state function**.

2.4.3 Standard enthalpy change, ΔH°

Enthalpy changes are dependent on the conditions of the reaction, including temperature, pressure and state (i.e. gas, liquid or solid). As with STP in gases, it is necessary to define a set of standard conditions, and enthalpy values given in tables are usually given for this standard state.

The **standard state** of a substance is defined as follows:

Temperature = 25 °C = 298 K
Pressure = 1 bar = 100 000 Pa = 100 kPa
State = the pure form of the substance.

The **standard enthalpy change, ΔH°**, of a substance is the enthalpy change of the substance in its standard state.

Do not confuse the standard state conditions in thermochemistry with the standard conditions of gases - they are different! Determine what the difference is, and remember it!

2.4.4 Thermochemical equations

A **thermochemical equation** is an equation which shows a balanced chemical reaction, with the associated change in enthalpy. It is vital that you understand how to interpret thermochemical equations.

Let's have a look at an example:

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)} \qquad \Delta H^\circ = -1203.6\ kJ$$

What can we tell from this thermochemical equation?

When 2 moles of solid magnesium and 1 mole of oxygen gas in their standard state react to form magnesium oxide, 1203.6 kJ of heat is given off to the surroundings. (ΔH° is negative, so the reaction is exothermic)

Enthalpy is an extensive property. This means that if we double the quantities of the reactants, then the amount of heat given off in the reaction will also double. If 4 moles of solid magnesium and 2 moles of oxygen gas in their standard state react to form magnesium oxide, 2 x -1203.6 kJ = -2407.2 kJ of heat is given off to the surroundings.

ΔH° is proportional to the amount of reactants in the balanced equation.

If we reverse the reaction, then the sign of ΔH° also changes. If 2 mol solid MgO dissociates to give 2 mol solid Mg and 1 mol O_2 gas, then 1203.6 kJ of heat will be absorbed from the surroundings (endothermic), and ΔH° will become ΔH° = 1203.6 kJ.

Lastly, the enthalpy change of a reaction depends on the state of the reactants and products (ie. solid, liquid or gas). If liquid oxygen, rather than oxygen gas, reacted with magnesium, the ΔH value would be different.

Thermochemical equations written without the phases of the reactants and products are meaningless!

Activity 2.1

Consider the reaction:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H° = -571.7\ kJ$

Will heat be given off or absorbed by the system?

How much heat is given off if 12.096 g H_2 (g) react with 95.996 g O_2 (g) to give liquid water at an atmosphere of 1 bar and a temperature of 298 K?

Hints: Always work in moles. The thermochemical equation gives ΔH°, not ΔH. Are the conditions given in the question standard?

2.5 Heat capacity and calorimetry

As we have already seen, ΔH can be determined in a laboratory by measuring the heat flow of a reaction at constant pressure. The heat flow causes a change in temperature, and this can be easily measured with a simple thermometer. The measurement of heat flow is called **calorimetry**.

Not all substances heat and cool at the same rate. For example, it is easier to heat a 50g chunk of iron metal than it is to heat a 50 g sample of water. This is because we have to put in more energy to heat the water than to heat the metal. To heat 1 g of iron by 1°C requires 0.45 J of energy, whereas it takes 4.18 J of energy to heat 1 g of water by 1°C.

The **heat capacity** of a substance is the amount of energy (heat) required to raise the temperature of the substance by 1°C.

The **molar heat capacity** of a substance is the amount of energy (heat) required to raise the temperature of 1 mol of the substance by 1°C.

The **specific heat capacity** of a substance is the amount of energy (heat) required to raise the temperature of 1 g of the substance by 1°C.

Therefore, in our example of iron and water, we can simply say that solid iron has a specific heat capacity of 0.45 $\frac{J}{g.°C}$ and water has a specific heat capacity of 4.18 $\frac{J}{g.°C}$.

Note that the units of specific heat capacity can be given in either $\frac{J}{g.°C}$ or $\frac{J}{g.K}$ because a *change* in temperature by 1°C is exactly the same as a *change* in temperature by 1 K.

Example: In Celsius, 26°C – 25°C = 1 °C, and in Kelvin, 299.15 K – 298.15 K = 1 K

Therefore, ΔT (°C) = ΔT (K).

So, we know that the specific heat capacity of a substance is the amount of heat energy (q) required to raise the temperature of 1 g of the substance by 1°C. The quantity of heat transferred is denoted by the unit q. We can write this as an equation as follows:

$$\text{Specific heat capacity (C)} = \frac{\text{quantity of heat transferred (q)}}{\text{grams of substance (g)} \times \text{temperature change (K or °C)}}$$

$$\text{Or simply:}\quad C = \frac{q}{m \times \Delta T}$$

When a sample gains heat (q is positive), the temperature of the sample increases (ΔT is positive). (If a sample loses heat, then q is negative.) The above equation rearranges to:

$$q = C \times m \times \Delta T$$

Using this equation, we can calculate the quantity of heat that a substance has gained or lost by using its specific heat capacity, together with the mass and temperature change which we have measured.

Sample Exercise 2.1

A 50.0g chunk of iron metal at 200 °C is dropped into 100 g of water, which is at 25.0°C. Assuming that all the heat lost by the iron is absorbed by the water (in other words, no heat is lost to the surroundings), calculate the final temperature of the iron and water. The specific heat capacity of solid iron is 0.45 J/g.°C and the specific heat capacity of water is 4.18 J/g.°C

Solution

We know that heat gained by the water is q, and the heat lost by the iron is –q. We also know that the final temperature of iron is the same as the final temperature of water. Since all the heat lost by the iron is gained by the water, we can write:

$$\text{Heat lost}_{\text{(Fe)}} = \text{Heat gained}_{\text{(Water)}}$$

$$-q_{\text{(Fe)}} = q_{\text{(Water)}}$$

But $q = C \times m \times \Delta T$, so:

$$-(C \times m \times \Delta T)_{\text{Fe}} = (C \times m \times \Delta T)_{\text{Water}}$$

$$-(C \times m \times (T_{\text{final}} - T_{\text{initial}}))_{\text{Fe}} = (C \times m \times (T_{\text{final}} - T_{\text{initial}}))_{\text{Water}}$$

Substituting our values into the equation gives:

$$-(0.45\ \text{J/g.°C} \times 50\ \text{g} \times (T_{\text{final}} - 200\text{°C})) = (4.18\ \text{J/g.°C} \times 100\ \text{g} \times (T_{\text{final}} - 25.0\text{°C}))$$

Now, all we need to do is multiply out, and then solve for T_{final}:

$$-22.5\ \frac{J.g}{g.°C} \times T_{\text{final}} + 4500\ \frac{J.g.°C}{g.°C} = 418\ \frac{J.g}{g.°C} \times T_{\text{final}} - 10450\ \frac{J.g.°C}{g.°C}$$

$$4500\ \text{J} + 10450\ \text{J} = (418\ \frac{J}{°C} + 22.5\ \frac{J}{°C}) \times T_{\text{final}}$$

$$14950\ \text{J} = 440.5\ \frac{J}{°C} \times T_{\text{final}}$$

Therefore, the final temperature of the water and iron is $T_{\text{final}} = 33.94$°C.

Activity 2.2

If you pour 40 g of refrigerated milk (at 4°C) into 200 g of freshly percolated coffee (at 96°C), what will the final temperature of your coffee be?

Assume that no heat is lost to the cup or to the surroundings.

$C_{(milk)} = 3.93$ J/g.°C and $C_{(coffee)} = 4.18$ J/g.°C

2.6 Hess's law

Hess's law states that if a reaction is carried out in a series of steps, ΔH for the reaction is the sum of ΔH for each of the steps.

Activity 2.3

Hess's law is a consequence of the fact that enthalpy is a state function.

Explain this statement.

Since enthalpy is a state function, it should be obvious that the total change in enthalpy for a reaction is independent of the number of steps. The total change of enthalpy is also independent of the nature of the reaction path. This means we can choose any series of reactions that we like, as long as we get from the reactants to the desired product. ΔH for the overall reaction will always be the same.

Sample Exercise 2.2

Consider the following reactions, which form the series of 3 steps required to produce NO_2 from NO:

(1) $O_{3(g)} \rightarrow \frac{3}{2}O_{2(g)}$ $\Delta H° = -142.3$ kJ

(2) $O_{2(g)} \rightarrow 2O_{(g)}$ $\Delta H° = +495.0$ kJ

(3) $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$ $\Delta H° = -198.9$ kJ

Calculate ΔH° for the overall reaction:

$NO_{(g)} + O_{(g)} \rightarrow NO_{2(g)}$

Solution

In order to use equations (1), (2) and (3), the first step is to arrange them so that $NO_{(g)}$ and $O_{(g)}$ are on the side of the reactants, and $NO_{2(g)}$ is on the side of the products of the reaction. To do this, we need to reverse (1) and (2). Remember to also reverse the sign of ΔH° for those two reactions:

$\frac{3}{2}O_{2(g)} \rightarrow O_{3(g)}$ $\Delta H° = +142.3$ kJ

$2O_{(g)} \rightarrow O_{2(g)}$ $\Delta H° = -495.0$ kJ

$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$ $\Delta H° = -198.9$ kJ

In the final equation, we want $O_{(g)}$, and not $2O_{(g)}$, so we have to divide (2) by 2. This means that we must also divide the relevant ΔH° value by 2. (Note that the $\frac{3}{2}O_{2(g)}$ in (1) can also be written as $\frac{1}{2}O_{2(g)} + O_{2(g)}$):

$\frac{1}{2}O_{2(g)} + O_{2(g)} \rightarrow O_{3(g)}$ $\Delta H° = +142.3$ kJ

$O_{(g)} \rightarrow \frac{1}{2}O_{2(g)}$ $\Delta H° = -247.5$ kJ

$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$ $\Delta H° = -198.9$ kJ

Add these three equations together and cancel out:

$\frac{1}{2}O_{2(g)} + O_{2(g)} \rightarrow O_{3(g)}$ ΔH° = + 142.3 kJ

$O_{(g)} \rightarrow \frac{1}{2}O_{2(g)}$ ΔH° = - 247.5 kJ

$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$ ΔH° = - 198.9 kJ

$$\cancel{\frac{1}{2}O_{2(g)}} + \cancel{O_{2(g)}} + O_{(g)} + NO_{(g)} + \cancel{O_{3(g)}} \rightarrow \cancel{O_{3(g)}} + \cancel{\frac{1}{2}O_{2(g)}} + NO_{2(g)} + \cancel{O_{2(g)}}$$

After cancelling: $NO_{(g)} + O_{(g)} \rightarrow NO_{2(g)}$

We must also add the ΔH° values.

So, for the overall reaction, ΔH° is:

$$\begin{aligned} \Delta H^\circ &= 142.3\ \text{kJ} - 247.5\ \text{kJ} - 198.9\ \text{kJ} \\ &= -304.1\ \text{kJ} \end{aligned}$$

Summary

You should now be able to apply thermo-chemical principles (temperature, heat and energy) when analyzing substances.

More specifically, you should be able to:

- Determine enthalpy as a measure of the amount of heat absorbed or released in a chemical reaction.
- Define and compare endothermic *versus* exothermic reactions.
- Define and calculate heat capacity.
- Define and apply Hess's law.

STUDY UNIT 3

Kinetics

3.1 Introduction

All chemical reactions take place at different speeds, or rates. The formation of a diamond may take millions of years, whereas a chemical explosion takes place in a fraction of a second. In modern times, the rate of reactions is of vital importance. The faster factories can produce chemicals, the more money they make. The speed of a reaction makes a difference to how fast a medicine has an effect in the body.

The study of the rates of chemical reactions is called kinetics. Theoretically, a lot of information can be gained by the study of kinetics. By studying rates of reactions under different conditions (for example, at different temperatures, or different pressures), we gain much insight into the mechanism of reactions; in other words, into the steps by which a reaction occurs.

By the end of this study unit, you will realize that the rates of both slow reactions, that take millions of years, and fast reactions, that take place in milliseconds, are all subject to the same basic principles.

3.2 Outcomes

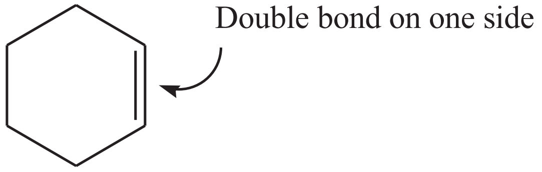
After studying this study unit you should be able to:

- Explain the conditions that are necessary for a reaction to occur.
- Explain how reaction rate depends on the frequency of collisions between molecules.
- Discuss the factors which affect the rate of a reaction.
- Explain what is meant by the rate of a reaction.
- Define rate law.
- Define the rate constant.
- Explain the order of reactions.
- Write rate laws for different orders of reactions.
- Interpret rate laws.
- Determine the units of the rate constant, k, for reactions of different orders.
- Explain the concept of activation energy.

3.3 Collisions

In order for a reaction to occur, two molecules must first collide. For example, a cyclohexene molecule cannot possibly react with a hydrogen bromide molecule if they do not collide. So a necessary condition for any reaction to occur is that the molecules taking part in the reaction must collide with each other.

It is important to understand that a collision does not necessarily mean that a reaction will take place. For example, in our example of cyclohexene reacting with hydrogen bromide, the reaction can only take place on the double bond side of the cyclohexene molecule. In other words, the orientation of the molecules must be right.



cyclohexene

There is one other necessary condition for a reaction to occur, i.e. the energy of collision. If the two molecules collide with not enough energy, no reaction will occur. We will have a look at the energy of collision (i.e. the activation energy) in more detail later in this study unit.

The key to understanding kinetics lies in the following statement - **The reaction rate depends on the frequency of collisions between molecules.** The greater the frequency of collisions, the greater the rate of the reaction. (But do not forget that this statement only applies if the collision occurs with **sufficient energy** and the **correct orientation** for the reaction to take place.)

3.4 Factors that affect reaction rates

There are four factors which affect the rate of a reaction:

- **The physical state of the reactants.**
  The more readily molecules collide with each other, the more rapidly they react. Intuitively, it should be obvious that reactions between liquids will occur fairly rapidly, whereas reactions between solids and liquids will depend largely on the surface area of the solid. With solids, reactions can only occur at the surface, so a larger surface area means faster reactions. Solids that are ground into a finer powder will therefore react faster with a liquid than one large chunk of the solid.

- **The concentration of the reactants.**
  The higher the concentration of the reactants, the more molecules there are in a given volume, and there is a greater chance of a collision. It is worth mentioning here that as a reaction progresses, the reactants are used up, and as their concentration decreases, the rate of the reaction also decreases.

- **The temperature at which the reaction occurs.**
  Increasing the temperature of a molecule increases its kinetic energy. As molecules move more rapidly, they collide more frequently, but also with more energy. Consequently, a higher temperature means faster reactions.

  This statement often causes confusion when we consider endothermic and exothermic reactions. When we talk about the rate of a reaction, we normally refer to the forward reaction. The rate of endothermic reactions will increase with an increase in temperature, but the rate of an exothermic reaction decreases as the temperature increases. However, this is easily understood by realizing that in exothermic reactions, there is still an increase in rate, but it is in the direction of the reverse reaction.

- **The presence of a catalyst.**
  Catalysts are agents that increase the rate of a chemical reaction without being consumed during the reaction. There are many ways in which they can do this: for example, by lowering the activation energy of a reaction, or by increasing the local concentration of reactants on a solid surface. In living creatures, enzymes are catalysts which increase the rate of specific biochemical reactions.

3.5 Reaction rates

The way in which we examine the rate of a reaction is to measure the change in concentration of a reactant or product as time passes.

$$\text{Rate} = \frac{\text{Change in Concentration}}{\text{Change in Time}}$$

Mathematically, this is written as

$$\text{Rate} = \frac{\Delta \text{Conc}}{\Delta \text{t}}$$

If we consider a reaction A → B, where a reactant A becomes product B, there are two ways of measuring the rate. Either we can measure the disappearance of the reactant, A, or we can measure the appearance of the product, B.

By convention, rates are always expressed as positive quantities, which means that we have to use signs to show whether something is disappearing or appearing.

As the product B forms, $\text{Rate} = \frac{\Delta[\text{B}]}{\Delta \text{t}}$, but as A disappears, $\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta \text{t}}$.
Note the negative sign! A negative sign reminds us that the rate is expressed as the disappearance of a reactant, and not as the appearance of a product.

Since the rate is measured as a change in concentration ($\frac{mol}{L}$) over change in time (s):

The units for the rate of a reaction are $\frac{mol}{L.s}$.

3.6 Rate laws and the rate constant

3.6.1 Rate laws

As you have already seen, as concentration increases, the rate of the reaction also increases. The rate is proportional to the concentration of a reactant, e.g. Rate $\propto$ [A], or a function of that concentration, e.g. Rate $\propto [A]^m$ (see section 3.6.3 below).

Mathematically, we can write this as:

$$\text{Rate} = k[A]$$

If the rate depends on the concentration of two reactants, A and B, then:

$$\text{Rate} = k[A][B]$$

The overall concentration dependence of a reaction rate is give as an equation called a **rate law.**

The proportionality constant, *k*, in a rate law is called the **rate constant**.

3.6.2 The rate constant, *k*

The rate constant changes with the reaction conditions of a particular reaction. In particular, the magnitude of *k* changes with temperature, and reflects how temperature affects the rate.

3.6.3 Orders of reactions

Very often, reaction rates of specific reactions are **experimentally** found to be proportional to the reaction concentrations raised to certain powers. For example, it may be found that, for a specific reaction, the rate depends on the concentration of A squared. (Rate = $k[A]^2$).

For a general reaction which has the rate law:

$$\text{Rate} = k[\text{reactant 1}]^{m}[\text{reactant 2}]^{n},$$

the exponents, m and n, are called **reaction orders**. The **overall order of a reaction** is the sum of all the exponents.

Note that reaction orders must be determined experimentally. They do not necessarily correspond to the stoichiometric coefficients in the balanced chemical equation!

We commonly encounter reaction orders of 0, 1 or 2.

(A zero order reaction is a reaction which does not depend on the concentration of any of the reactants, provided that at least some of the reactants are present.)

Sample Exercise 3.1

The experimental rate law for the reaction $6A + B \rightarrow 5C + D$ is:

Rate = $k[A][B]^4$

(i) What is the overall order of this reaction?

(ii) If the concentration of A is tripled, what happens to the reaction rate?

(iii) If the concentration of B is doubled, what happens to the reaction rate?

Solution

(i) The overall order is 1 + 4 = 5.

(ii) If [A] is tripled, the reaction rate will increase by $3^1 = 3$ times

(iii) If [B] is doubled, the reaction rate will increase by $2^4 = 16$ times.

3.6.4 Units of the rate constant

Units of the rate constant depend on the overall reaction order.

For example, for a first order reaction:

Rate = k[A], so the units are:

$$\text{Rate}\left(\frac{\text{mol}}{\text{L.s}}\right) = \text{k} \times [\text{A}]\left(\frac{\text{mol}}{\text{L}}\right)$$

$$\therefore \text{k} = \text{s}^{-1}$$

For a second order reaction:
Rate = k[A]^2, so the units are:

$$\text{Rate}\left(\frac{\text{mol}}{\text{L.s}}\right) = \text{k} \times [A]^2\left(\frac{\text{mol}}{\text{L}}\right)^2$$

$$\therefore \text{units (k)} = \frac{\text{L}}{\text{mol.s}}$$

Activity 3.1

For the reaction:

$2H_{2(g)} + 2NO_{(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$,

the observed rate law is: Rate = $k[NO]^2[H_2]$

(i) What is the order of the reaction with respect to NO?

(ii) What is the order of the reaction with respect to H_2?

(iii) What is the overall order of the reaction?

(iv) Determine the units of k assuming time in seconds and concentrations in mol/L.

3.7 Introduction to activation energy

As we have already mentioned, molecules must possess a minimum amount of energy in order to react. In order for a reaction to occur, the electron clouds of the reactants must interact in such a way that electronic rearrangements occur, and new bonds are formed. If the reactants have insufficient energy, the electron clouds will repel each other, and no reaction will occur. This minimum amount of energy needed for the reaction to occur is called the **activation energy, E_a.** The rate of a reaction depends on the magnitude of the activation energy. The lower the activation energy, the faster a reaction will occur.

A **catalyst** will speed up a reaction. It increases the rate constant, *k*, either by increasing the frequency of collisions or by lowering the activation energy, E_a.

Activity 3.2

Explain why the frequency of collisions is not the only factor affecting a reaction rate.

Summary

You should now be able to determine the rate and establish the order of reactions.

More specifically, you should be able to:

- Explain the concept of rate, rate law and rate constant.
- Determine rates, orders of reactions and rate constants.
- Explain activation energy.

Part 2

Introductory Organic Chemistry

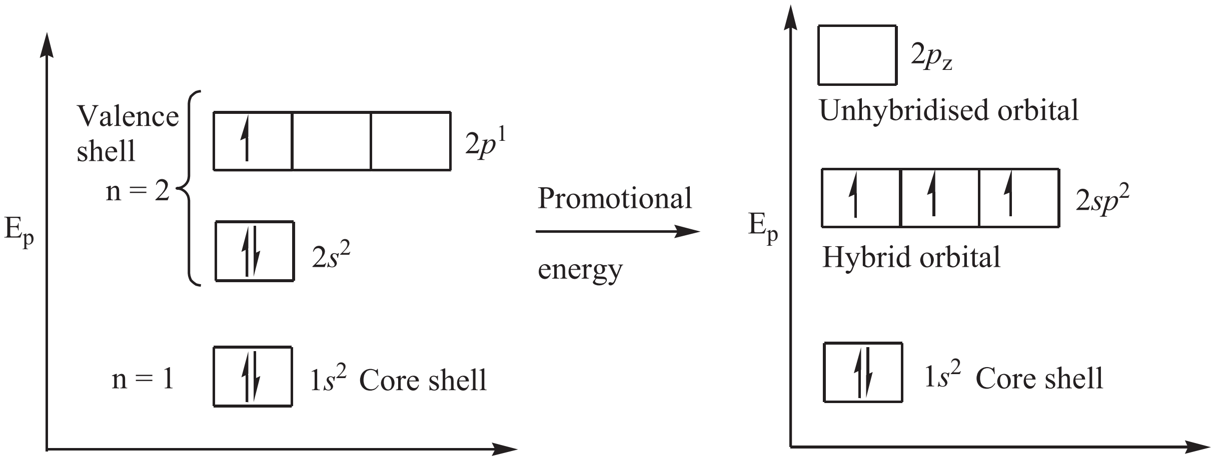
Organic chemistry, previously referred to as the chemistry of life, is perhaps best defined as the chemistry of carbon–containing compounds. Organic chemistry often studies life by making new molecules that give information not available from the molecules actually present in living systems. The agents of organic chemistry (molecules) and their behaviour (reactions) can be described by a powerful and beautiful graphical language, consisting of two- and three-dimensional chemical formulas that express the atoms, bonds, electrons, charges and geometries that characterize their structure. Indeed, this formula notation is so powerful that organic chemists can tell at a glance much about the chemistry and reactivity of a molecule and even how it might be made from simpler substances.

STUDY UNIT 4

An Overview of Chemical Bonding

4.1 Hybridization

Hybridization involves the promotion of a valence electron from the lower energy orbital to the higher energy orbital resulting in the fusion of the orbitals involved. For example, an sp^3 hybrid orbital is made up of one s orbital and three p orbitals; the sp^2 is made up of one s and two p orbitals and the sp hybrid orbital is made up of one s and one p orbital. The hybrid orbital has energy between the fusing orbitals in the ground state. Unhybridized orbital(s) has(ve) energy higher than the hybrid orbital. Take boron, for example, in the ground state B has two electrons in the core shell (the one next to the nucleus) and three valence electrons in the valence shell. Two of those electrons are in the 2s orbital and one in the $2p_x$ orbital and the other two p orbitals (p_y and p_z) are empty. Promotion of one electron from the 2s orbital into the p_y orbital leads to formation of a $2sp^2$ hybrid orbital and the remaining p_z orbital is empty and lies highest in energy.



Ground state electron configuration

Hybrid state

When B reacts with three atoms of fluorine to form boron fluoride (BF_3) each fluorine atom contributes a single electron that pairs the spin with one of the electrons in the sp^2 orbital of boron. The remaining p_z orbital on B in BF_3 is empty and it is responsible for the Lewis acidity of boron fluoride.

Activity

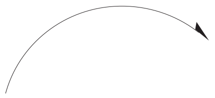
Follow the above example and show how C, N and O can be hybridized to sp^3, sp^2 and sp states. **Note:** label orbitals as core shell, hybridized and unhybridized.

4.2 Types of Bonds (The noble-gas configuration and electronegativity)

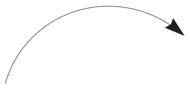
In any chemical reaction, atoms either gain or lose one or more electrons to attain the noble gas configuration. Chemical reactions (bond formation or breakage) involve the movement of valence electrons from a region of high electron density to a region of less electron density. The concept of electronegativity (i.e. the tendency of an atom to attract to itself a pair of bonding electrons in a **molecule**) plays a significant role in any chemical reaction. In any chemical reaction, the more electronegative elements (mostly non-metals) tend to gain electrons to attain the noble-gas configuration while electropositive elements (e.g., metals) tend to lose electrons to attain the noble gas configuration.

4.3 Movement of electrons during bond formation or breakage

Bond formation and bond breakage involve the movement of either one or two electrons (**note**: only electrons move). The movement of electrons is illustrated by either a half-headed curved arrow or full-headed curved arrow. Each half of the arrow represents a single electron and the curved line represents movement of the electron(s).



Half-headed curved arrow
Movement of a single electron



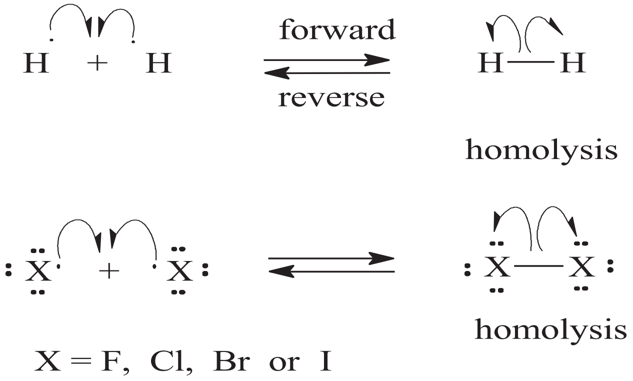
full-headed curved arrow
Movement of two electrons

4.4 Formation and breakage of non-polar covalent bonds

A non-polar covalent bond forms between atoms of similar electronegativity. For example, when one electron from each hydrogen atom is involved in the bond formation to form hydrogen molecule, we use a half-headed curved arrow to illustrate the movement of electrons (forward reaction). Elements comprising a diatomic molecule of similar atoms are held together by a covalent bond in which the bond pair electrons are equally shared between the two atoms (H_2, N_2, O_2, X_2 where X is a halogen). The two atoms comprising a hydrogen molecule (H_2) or halogen molecule (X_2), for example, have equal electronegativity and therefore the bond pair electrons between them are equally shared and the entire molecule is non-polar. It is important to note that although there are only two electrons, when counting electrons belonging to each element in H_2, the bond pair electrons form part of the total count per hydrogen atom. This simply means that the bond pair electrons belong equally to either atom, i.e., each hydrogen has two electrons to itself.

When two similar halogen atoms (X = F, Cl, Br or I) react to form diatomic molecules (X_2) each element in the molecule has eight of electrons around itself. It is important to note that although there are only two electrons in the bond, when counting electrons around each element in X_2, the bond pair electrons form part of the total count per halogen atom, i.e. eight electrons. It is very important to note that equal sharing in chemical terms does not mean dividing into equal halves, but to have equal ownership at any given time. *It is important to note that the bond (–) in any molecule or ion denotes two electrons.*

Examples of non-polar covalent bond- formation and breakage:

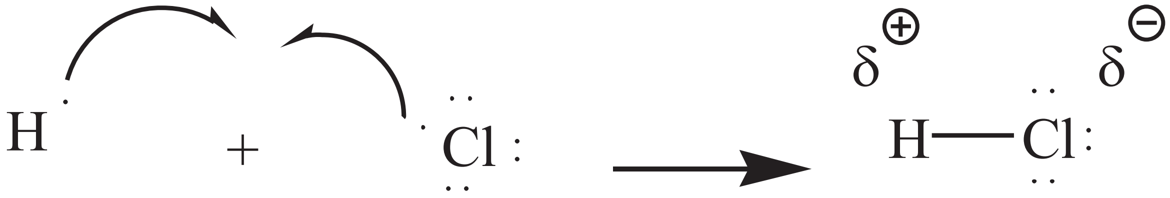


When either hydrogen molecule or halogen molecule breaks or cleaves into two elements, each atom gains a single electron and we illustrate the movement of these electrons during bond breakage by half-headed curved arrows moving from the middle of the bond to the respective atom (reverse reaction). This type of bond cleavage is called homolysis or homolytic bond cleavage.

4.5 Formation and breakage of polar covalent bonds

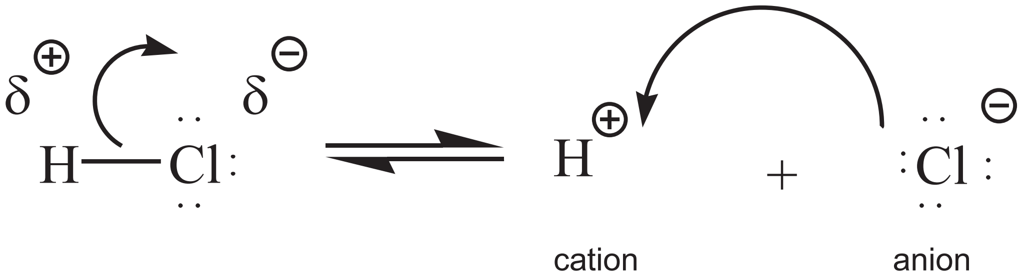
When two elements (non-metals) of different electronegativity react to form a bond, each atom contributes one electron to the bond pair. We use half-headed arrows that meet in between the two atoms to illustrate the movement of electrons (forward reaction). When bonded together to form a molecule, the situation changes and the atom of high electronegativity pulls the bond pair electrons towards itself rendering the less electronegative element electron-poor. The electron density becomes concentrated largely closer to the more electronegative atom, leaving the other element of less electronegativity electron poor or deficient. As a result the bond becomes polarized (positive and negative poles) with the atom of high electronegativity attaining a partially or slightly negative charge (represented as δ^-) and the one with less electronegativity becoming slightly or partial positive (represented as δ^+). Such a covalent bond in which the bond pair electrons are attracted towards the atom with high electronegativity is termed a polar covalent bond.

Example of polar covalent bond formation:



Polar covalent bonds are formed mostly between non-metals. When we count electrons around each element, the bond pair electrons form part of the total count per atom. For example, in H-Cl, there are two electrons around hydrogen (these are the bond pair electrons) and eight electrons around chlorine atom (these are the three pairs of nonbonding electrons and the bond pair electrons).

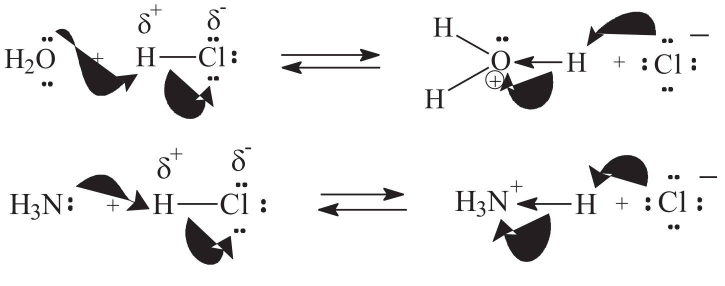
When in turn a polar covalent bond breaks, both bond pair electrons are then taken away by the atom of high electronegativity. To illustrate this type of bond cleavage, we use a full-headed curved arrow to illustrate the movement of two electrons from the middle of the bond over to the atom of high electronegativity (forward reaction). This type of bond cleavage where both bond pair electrons are taken away by the more electronegative atom is termed heterolytic bond cleavage or heterolysis.



When separated, the atom of high electronegativity gains a pair of electrons to become fully negatively charged ion (anion) and the less electronegative atom becomes fully positively charged (cation). When an anion and a cation of a non-metals react, the more electron rich ion (anion) is the one that attacks the electron-poor ion (cation) to form a polar covalent bond (see the reverse reaction).

4.6 Formation and Breakage of a Coordinate or dative covalent bond

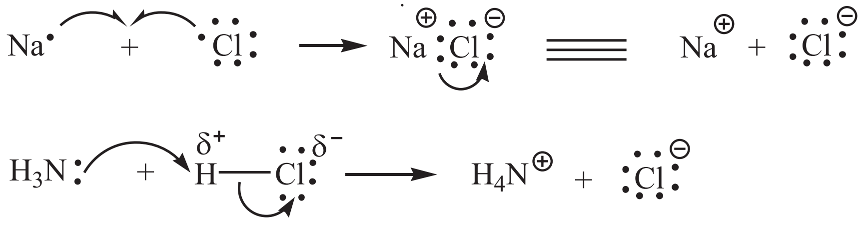
When water reacts with hydrochloric acid to form a hydronium ion (H_3O^+), both bond pair electron are contributed by the oxygen atom of water. In this association, oxygen is still in a noble gas configuration (octet state), however, it becomes fully positively charged. The bond between oxygen and the third hydrogen is termed a coordinate or dative covalent bond (shown in this case as an arrow between O and H). Note that in the HCl below, the chloride ion serves as a counter ion to give the hydronium ion a zero net charge. Also note that in the Lewis structure of hydronium ion, oxygen has only one pair of non-bonding electrons and therefore has a positive charge. A dative or coordinate covalent bond also forms between nitrogen of ammonia and hydrogen from the hydrochloric acid in ammonium chloride (shown in this case as an arrow between N and H).



When a coordinate covalent bond breaks (reverse reaction), the bond pair electrons are retained by the atom of high electronegativity, which is the one that initially donated them to form this bond. A full-headed curved arrow is drawn from the coordinate covalent bond to an atom of high electronegativity in the association. In this case, the atom that gains a pair of electrons becomes neutral and the other component from the broken bond associates with the counter ion (anion) to form a neutral molecule (e.g., HCl).

4.7 Formation and Breakage of Ionic Bonds

An ionic bond involves an electrostatic attraction of two oppositely charged ions. It is usually formed between a metal (electropositive) and a non-metal (electronegative). Sodium and chlorine atoms react to form sodium chloride. Since halogens have high electronegativity and metals are electropositive, the bond pair electrons are taken away by chlorine atom rendering it a negatively charged chloride ion (anion). On the other hand, sodium becomes positively charged (cation). It is important not to confuse a polar covalent molecule (partial positive and partial negative) with an ionic compound (fully positive and fully negative charges). The association between ammonium ion (NH_4^+) and chloride ion (Cl^-) or between hydronium ion (H_3O^+) and chloride ion also involves an ionic bond.



In both ions, the affected atoms attain the noble gas configuration with either a completely filled (anion) or a completely empty (cation) valence level.

4.8 Lewis structures

It is important to always write the Lewis structures of molecules (line/dot formulas) representing bond pair electrons by a line and non-bonding electrons (single or paired) by dots. When a molecule has a polar bond indicate bond polarity with partial negative

(δ^-) and partial positive (δ^+) charges. On the other hand, for ionic species attach a positive charge to the respective atom in the cation (e.g. O in hydronium ion or N in ammonium ion) and a negative charge to the respective atom in the anion (e.g. O in hydroxide ion). At this stage the knowledge of formal charges is assumed and you are not expected to put charges outside brackets, but on the respective atom in a molecule or compound.

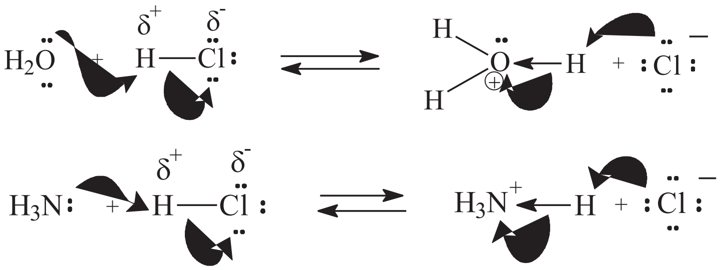
Activity

Draw the Lewis structures of the following species

(a) Ammonia
(b) Hydrochloric acid
(c) Hydronium ion
(d) Boron trifluoride
(e) Nitric acid
(f) Sulfuric acid.

4.9 Acid-Base Reactions

An acid-base reaction involves the movement of electrons from a base (electron rich) to an acid (electron poor). When ammonia reacts with hydrochloric acid, the lone pair electrons on the nitrogen atom of ammonia attacks the electron poor hydrogen atom of HCl (polar covalent). At the same time chlorine which is more electronegative than hydrogen takes the bond pair electrons and become fully negative. Remember that HCl is a polar molecule with a partial positive charge on chlorine (why?) and a partial positive charge on hydrogen (why?).



Since nitrogen has used its lone pair electrons to attack the hydrogen of HCl, it now becomes fully positive in its octet state (noble gas configuration). What do we call the new bond formed between N and H? What do we call the association between the ammonium ion and chloride ion?

4.10 Electron delocalization and resonance structures

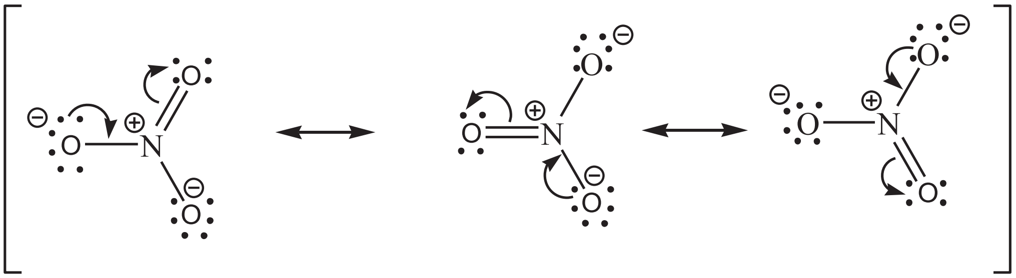
Electrons can be delocalized in a step-by-step fashion over three, four or more atoms to form resonance structures. Electron delocalization involves formation of alternating double and single bonds through the movement of pi bond or non-bonding electrons. It is important to note that a double bond comprises of a strong Sigma (σ) bond and weak pi (π) bond. There are several points to note when writing resonance structures:

- Resonance structures are enclosed in square brackets and separated by a double-headed arrow.
- In going from one resonance to the other, no atom can change position; only lone electrons and π (pi) bond electrons can move. When there is a combination of either a charged electron pair or neutral (single or paired) electrons and π bonds, negatively charged lone pair electrons move more easily (faster) than a neutral single or lone pair, which in turn move faster than π electrons. Sigma (σ) bonds do not move during resonance hybrid transformations.
- Electrons move from an atom to a bond and from a bond to an atom or bond, they cannot jump over to other atoms. A pair of electrons move from an atom (neutral or negatively charged) to the adjacent σ bond to form a double bond (new bond being a π bond) or from a π bond to the adjacent atom which may become neutral (if

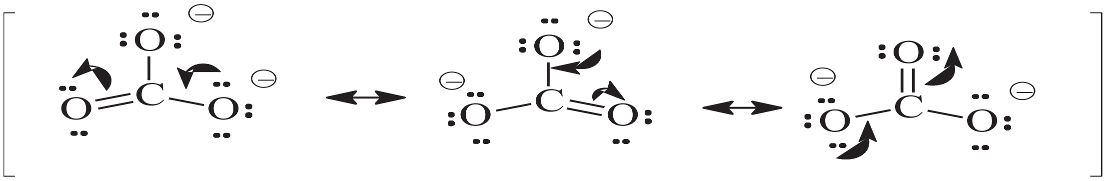
previously positive) or negatively charged (if previously uncharged). The negatively charged atom may then form a π bond with the adjacent atom.

- There should be no more than eight electrons (not more than four bonds) around any second period elements (carbon, nitrogen or oxygen).
- Negative charges prefer to be on the more electronegative atom, with positive charges on the more electropositive atoms.

In the resonance structures of nitrate (NO_3^-) and carbonate ions (CO_3^{2-}) each oxygen atom at some stage had a double bond character or a negative charge as shown below. A pair of electrons moves from the electron-rich oxygen atom (i.e. the negatively charged oxygen) to form a double bond with either nitrogen or carbon. At the same time as the new double bond is formed, the other bond (pi bond) of the old double bond breaks with electron pair going to oxygen (why?) so that the central atoms retains a noble gas configuration (octet state in the case of C and N).



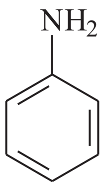
Nitrate ion

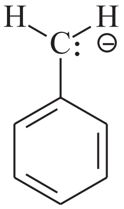


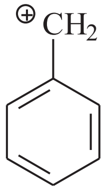
Carbonate ion

Activity

Use the appropriate curved arrows (half-headed or double-headed) to illustrate the movement of electrons when converting the resonance structures of the following species

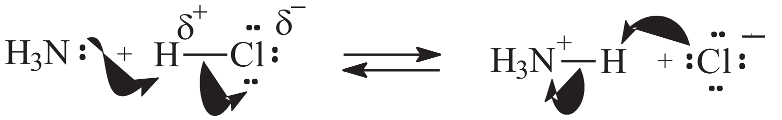






4.11 What is a Reaction Mechanism?

A reaction mechanism is a step-by-step representation of electron movement during bond formation and/ or breakage, whereby electron movement is illustrated by single-headed or double-headed curved arrows. An acid-base reaction, for example, involves the movement of electrons from a base (electron rich) to an acid (electron poor). Note that hydrogen can only accommodate a maximum of two electrons, hence when it gains a pair of electrons from N it has to lose the bond pair electrons to Cl.



Base Acid Conjugate acid conjugate base

In the reverse reaction, the chloride ion which is electron rich abstracts a proton from ammonium ion to form ammonia and HCl. As the chloride ion abstracts a proton from the ammonium ion in the reverse reaction, at the same time the bond between N and H breaks with the more electronegative N atom taking the pair with it.

Summary

You should now be able to explain fundamental concepts related to chemical bonding.

More specifically, you should be able to:

- Draw resonance structures. Define and compare endothermic *versus* exothermic reaction*s.*
- Draw mechanisms of delocalization of electrons when converting one resonance hybrid to the other.

STUDY UNIT 5

Hydrocarbons – Structure, Nomenclature, Reactions

5.1 What are hydrocarbons?

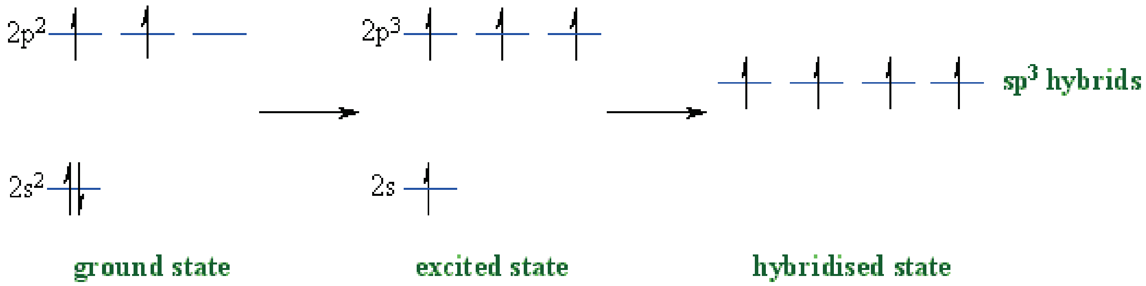
Hydrocarbons are organic compounds made up of carbon and hydrogen atoms only. These are divided into two main groups according to the type or nature of bonds between carbon atoms. Saturated hydrocarbons have single bonds around each carbon atom and examples include alkanes and cycloalkanes. Unsaturated hydrocarbons contain one or more double or triple bonds between two carbon atoms. Examples of unsaturated hydrocarbons include alkenes and cycloalkens, alkynes and aromatic compounds (benzene derivatives).

5.2 Generalized description of alkane structure

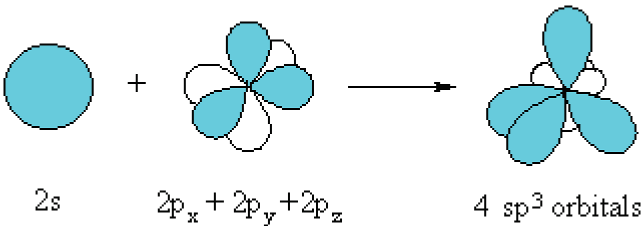
Alkanes are characterized by C-C and C-H single bonds and each carbon of an alkane is sp^3 hybridized (see Study Unit 4 above) and bonded to four other atoms (C or H) by single covalent bonds (sigma). The bond angles (C-C-C or C-C-H) around each carbon are 109.5˚ and the geometry around each carbon is tetrahedral.

Hybridization of C in alkanes

Let us see how carbon (electron configuration $1s^22s^22p^2$) is **hydridized** to sp^3 state to account for the formation of four equivalent single bonds around C in alkanes.



- One electron is promoted from 2s to $2p_z$ to create an excited state (step 1)
- The four sp^3 hybrid orbitals have equal energy which lies in between the ground s and p state orbitals (step 2)
- The sp^3 hybrid orbitals have 4 unpaired electrons which can form 4 single bonds



The sp^3 hybrid orbital looks like a "distorted" p orbital with unequal lobes.

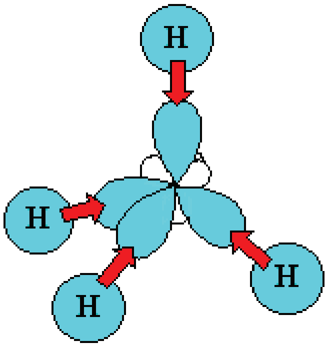
The 4 sp^3 hybrids point towards the corners of a tetrahedron.

The energy of the hybrid orbitals is therefore more stable.

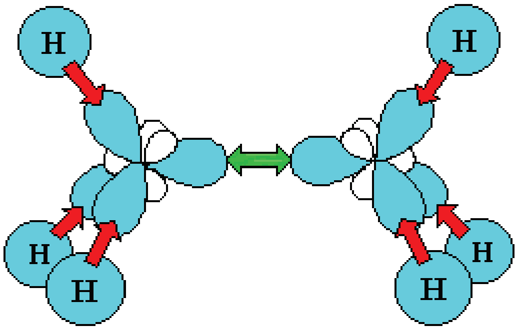
The structures of methane (CH_4) and ethane (CH_3–CH_3) below illustrate the structure of alkanes in detail:

Methane:

4 equivalent **C-H** bonds can be made by the interactions of sp^3 orbital of C with a 1s orbital of four H atoms



- **Ethane**, $H_3C\text{-}CH_3$:
- Both C are sp^3 hybridized.
- 6 **C-H** bonds are made by the interaction of sp^3 orbital of two C with 1s orbital of the six H atoms (see the arrows)
- 1 **C-C** bond is made by the interaction of the remaining sp^3 orbital of C with the remaining sp^3 orbital of the other C (see the double arrow)



Ethane can be used as a model for other higher chain alkane structures.

Alkanes are represented by the generalized molecular formula C_nH_{2n+2} where n is the number of carbon atoms.

Activity

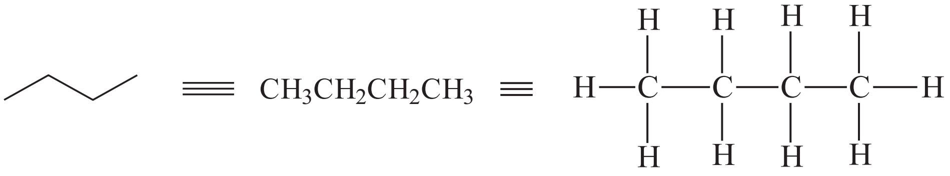
Write the molecular formula of an alkane with 110 carbon atoms.

5.3 How to draw structures of alkanes

We use either a line representation, condensed or branched structural formulas. At this level of study, learners are advised to master and restrict themselves to line and branched structural formulas.

Line representation

In a line representation of hydrocarbons, each tip or angle (corner) represents a carbon atom and the other atoms which are not shown are the hydrogen atoms. Note that around each carbon atom there are four bonds (therefore 8 electrons) to complete the noble gas configuration (octet state).



$\equiv CH_3CH_2CH_2CH_3 \equiv$

Line condensed branched

Branched structural formulas

Each carbon atom in a molecule is surrounded by four single bonds attached to carbon or hydrogen atoms. A bond is made-up of two electrons and therefore each carbon atom with four single bonds around itself is in octet state. To avoid mistakes later when proposing reaction mechanisms, it is best to always use the branched structural formulae.

5.4 IUPAC rules for naming alkanes

The International Union of Pure and Applied Chemists (IUPAC) rules have been designed and agreed upon internationally to standardize the names of straight-chain (or normal) and branched alkanes and other molecules belonging to other functional groups. Learners are expected to apply the relevant rules to construct the names from structures and *vice versa*. The rules below will be adapted and applied in modified forms to other functional groups and will not be revisited.

Normal or straight-chain alkanes

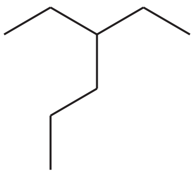
Make sure that you know all the names and how to draw line and branched structures of the first ten straight-chain alkanes (methane to decane).

Branched alkanes and constitutional/ structural isomers

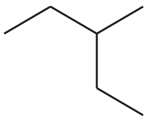
The names of the branched alkanes are based on those of straight chain alkanes and their names follow the IUPAC rules listed below.

(i) Longest continuous carbon chain

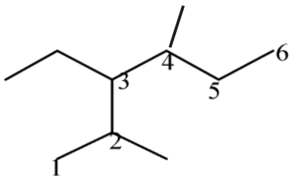
For branched alkanes, identify the **longest continuous carbon chain** in the molecule and this becomes the parent chain which gives the name to the alkane (**Note:** The longest continuous carbon chain is not necessarily linear). If there are two or more longest continuous carbon chains of equal lengths/ size, the chain with the most branches becomes the parent chain.



hexane > pentane



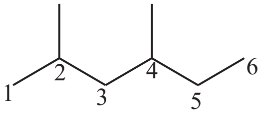
pentane > butane



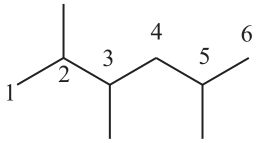
many branches : 2,4- dimethyl and 3-ethyl

(ii) Numbering of carbon atoms on the longest continuous carbon chain

Number the carbon atoms on the longest continuous carbon chain starting from the end nearest to the first branch. In the first molecule below, for example, there are two branches (methyl groups) on the hexane chain. Starting from the left, the first branch (methyl group) is at carbon number 2 while starting from the right, the first branch is at position 3 of the longest continuous carbon chain. Thus we number the longest continuous carbon chain starting from the left hand side because the first branch is nearer (position 2) from the left hand side. In the second molecule below starting from the left or the right, we have the methyl group at position 2, i.e., the two methyl groups are equidistant. In this case we number the chain in such a way that the third (middle) methyl group takes the lowest whole number from either end of the chain. This methyl group is at position 3 is nearer to the left than to the right hand side where it is at position 4. Longest continuous carbon chain in both cases is made up of six carbons and it is therefore hexane



hexane
2,4-dimethyl



2,3,5-trimethyl not
2,4,5-trimethyl

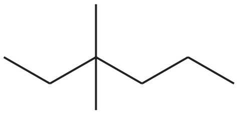
(iii) Branches and their positions on the longest continuous chain

The alkyl groups are distinguished from the parent molecules by the lack of a hydrogen atom and their names have the suffix (end) yl [meth**yl**, eth**yl**, prop**yl**, *etc*.). Their general formula is C_nH_{2n+1}. The branches may themselves be branched (see below) and their position on the longest continuous carbon chain are designated by a whole number (1, 2, 3, *etc*) separated from the branch name by a hyphen (-). For example, in the following molecule the longest continuous carbon chain is made up of three carbon atoms and has a methyl group on carbon number 2:

The parent chain is propane and the branch/ substituent is methyl. The branch name is separated from its positions as follows: 2-methyl. Two branches (similar or different) may occur on the same carbon (i.e., same position) and the position for each substituent should be indicated.

(iv) Use of prefixes for substituents and the numbering

The same branch may occur two, three, four, five times, *etc*., along the longest continuous carbon chain and we use prefixes: di, tri, tetra, penta, *etc*. The positions of each branch should also be indicated. Two methyl groups on the same carbon in the molecule below are designated as 3,3-dimethyl. Note that the numbers designate the positions of each methyl group on the longest continuous carbon chain and the numbers are separated from each other by a comma (,) and from the alphabet by a hyphen (-).



3,3-dimethyl

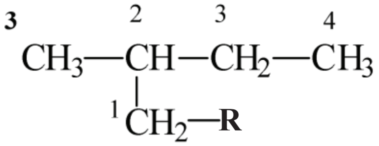
(v) Alphabetical order rule

Substituent names generally appear before the parent name of an alkane and are arranged in alphabetical order. Prefixes such as di, tri, tetra, *etc*, are not considered under alphabetical order. For example, di**m**ethyl comes after **e**thyl because **e** precedes **m** in alphabetical order list.

(vi) Names of branched alkyl groups

The IUPAC names of alkyl groups are derived from the names of the respective alkanes with the suffix –ane being replaced by the –**yl**. The carbon atom through which a branched alkyl group attaches to the longest continuous carbon chain (parent name of the entire molecule) is numbered C-1. Counting from this carbon we then identify the longest continuous carbon chain of that branched chain and this becomes the parent chain of the alkyl group. For example, the IUPAC name of the isopropyl group is 1-methylethyl. The entire branch is attached through C-1 at position 3 and therefore it becomes 3-(1-methylpropyl).

In the example below, the longest continuous carbon chain of the alkyl group is made up of four carbons (because 3 < 4) with a methyl group at carbon 2 relative to carbon 1 through which the entire group attaches to the parent molecule **R** (molecule ≠ branch), therefore **2-methylbutyl**.



$$\overset{3}{CH_3}-\overset{2}{\underset{\underset{{}^{1}CH_2-\mathbf{R}}{|}}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

The entire name of the branched substituent is enclosed in brackets ( ) and its position comes before the first bracket and is separated from it by a hyphen: number-(name). The names of branched substituents also follow the alphabetical order rule. For example, (1-methyl**e**thyl) precedes (1-methyl**p**ropyl) because **e** comes before **p** in alphabetical order list.

Activity

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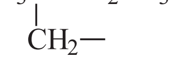
1. Write the IUPAC name for each of the following alkyl groups:

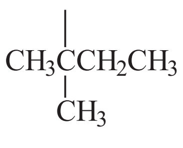


$CH_3\underset{\underset{CH_2-}{|}}{CH}CH_2CH_3$

A

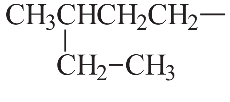
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2-$

B



$CH_3\overset{|}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_3$

C



$CH_3\underset{\underset{CH_2-CH_3}{|}}{CH}CH_2CH_2-$

D

2. Draw the structural formula for each of the following compounds:

4-(2-methylpropyl)octane; 5-(2,2-dimethylpropyl)nonane; 4-(1-methylethy)heptane

3. Draw the structures that correspond to the following names, apply the IUPAC rules for nomenclature to criticize the names and then provide the correct IUPAC names:

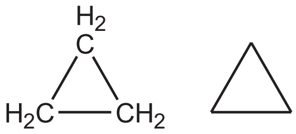
   2,6-diethylheptane; 3,4,6-trimethyl-5-ethylheptane

Note that the above rules can be modified and adapted to various functional groups (alkenes, alkynes, and substituted hydrocarbon derivatives, etc). Thus it is important to master the above concepts first before proceeding to other functional groups.

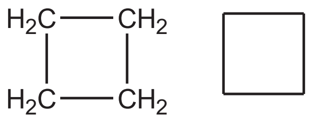
5.5 Generalized description of cycloalkane structures

Cycloalkanes are alkanes with their carbon atoms arranged in a ring. They have two less hydrogens than a noncyclic alkane with the same number of carbons. Cycloalkanes are named by using similar rules, but the prefix **cyclo**- immediately precedes the name of the parent alkane.

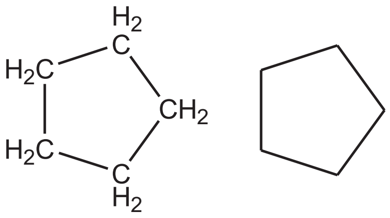
Since cycloalkanes consist of rings of -CH_2- units, they have a general formula $(CH_2)_n$, or C_nH_{2n}, and are also represented by polygons in skeletal drawings (line structures).



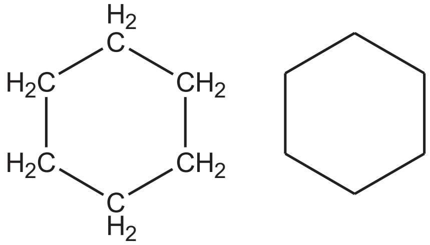
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

Rules for naming cycloalkane

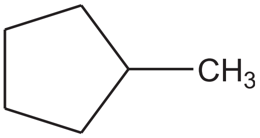
The rules for naming cycloalkanes are similar to the rules for naming noncyclic alkanes.

(i) **Identify the parent cycloalkane**

Count the number of carbon atoms comprising the ring and use the parent name for that number of carbons. Add the prefix **cyclo-** to the parent name.

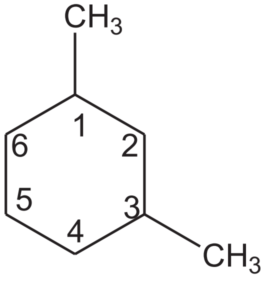
(ii) **Naming and numbering the substituents**

There is no need to number the position of a single substituent on a ring. For rings with more than one substituent, begin numbering at one substituent and proceed around the ring clockwise or anti-clockwise so that the second substituent has the lower number, i.e., is closest to the first substituent.



Methylcyclopentane

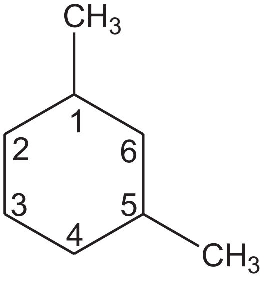
Numbering clockwise



1,3-dimethylcyclohexane

NOT

Numbering anti - clockwise

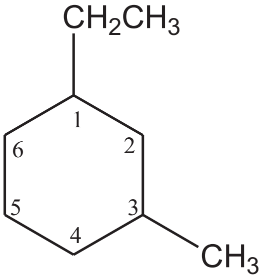


1,5-dimethylcyclohexane

The second substituent

has a lower number

With two different substituents, number the ring to assign the lowest numbers to the substituents alphabetically



Ethyl group at C1

Methyl group at C3

1-ethyl-3-methylcyclohexane

Activity

---

1. Draw structures corresponding to the following IUPAC names:

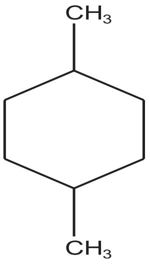
   1,1-Dimethylcyclooctane

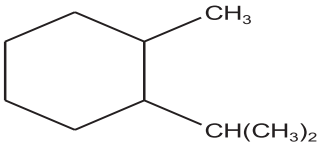
   3-cyclobutylhexane

   1,2-dichlorocyclopentane

   1,3-dibromo-5-methylcyclohexane

2. Give IUPAC names for the following cycloalkanes





5.6 Types of carbon atoms

Carbon atoms can be classified as primary (1°), secondary (2°), tertiary (3°) or quartenary (4°) depending on the number of carbon atoms attached to that specific carbon. Primary (1°) carbon is a carbon atom bonded to only one other carbon. Secondary (2^0) carbon is a carbon atom bonded to two other carbon atoms. A tertiary (3^0) carbon is a carbon atom bonded to three other carbons. Finally, a quaternary (4^0) carbon is bonded to four other carbon atoms.

Activity

Write the line structure of 2,2,3-trimethylbutane and then identify each carbon as 1°, 2°, 3°, or 4°.

5.7 Isomers

Isomers are compounds with the same molecular formula (composition) but different structural formulas. There are several types of isomers and some of the examples will be described later under the section Introduction to Stereochemistry.

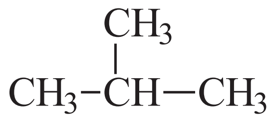
5.7.1 Structural isomers

These differ in the sequential arrangement of atoms or groups of atoms. Because they have different structures, structural isomers also have different names, different physical properties and in some cases different chemical properties. Butane (C_4H_{10}), for example, has two structural isomers:

$CH_3CH_2CH_2CH_3$

Butane (n-butane)

b.p. = -0.5˚C; m.p. = -135˚C



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

2-Methylpropane (isobutene)

b.p = -10˚C; m.p = -145˚C

Activity

Draw the structures and provide the IUPAC names of all the structural isomers of hexane

---

5.7.2 Conformational isomers

Conformational isomers (also known as conformers) can be interconverted by internal rotation about a C–C single bond. They can be represented by the Newman projection or sawhorse representation.

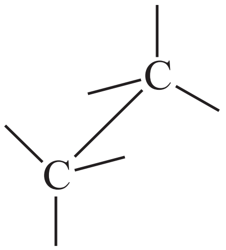
In a Newman projection, the carbon far away from the observer is represented by a circle and the one attached to it and closer to the observer by a solid dot (it is as if you look at the C–C bond at a 90° angle – i.e. vertically to the plane of the paper). The other three bonds on the carbon closer to the observer (solid dot) are represented by a symbol Y (at a 120° angle) with the solid dot at the centre. For the carbon far away from the observer (circle), the bonds start from the outside of the circle also resembling figure Y (upright or inverted).

Newman projections

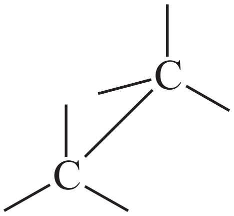
Gauche
Reduced bond pair–bond pair repulsion

Eclipsed
Increased bond pair–bond pair repulsion

Sawhorse representation



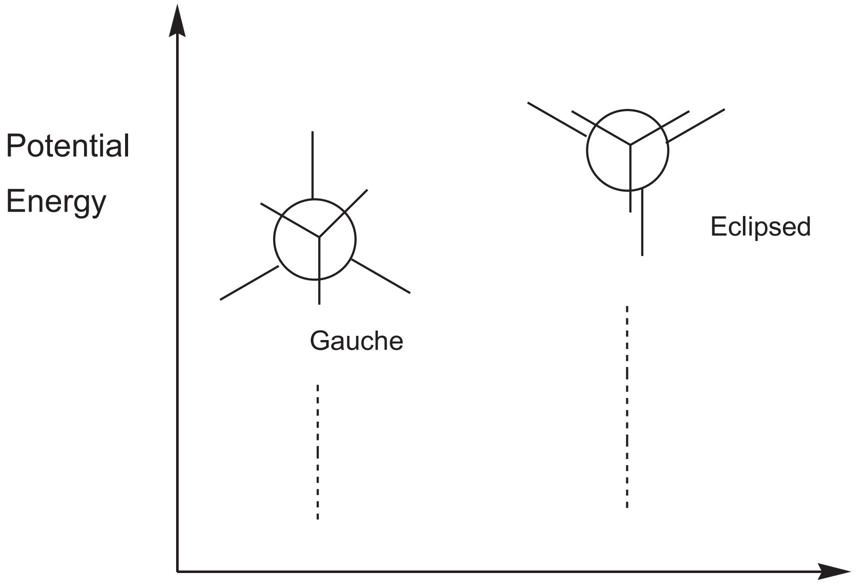
Gauche
Reduced bond pair–bond pair repulsion



Eclipsed
Increased bond pair–bond pair repulsion.

A comparison of the relative energies and stabilities of related conformers requires a thorough knowledge of the valence shell electron pair repulsion (VSEPR) theory. Lone pair or bond pair electrons prefer to be as far apart as possible so as to minimize forces of repulsion. Due to steric hindrance (i.e. repulsion due to size of groups or substituents attached to C atoms), substituents (atoms other than hydrogen) also prefer to be far apart to minimize forces of repulsion due to size.

Relative energies and stabilities of related conformers can be compared by means of potential energy *versus* conformational changes diagram as shown below.



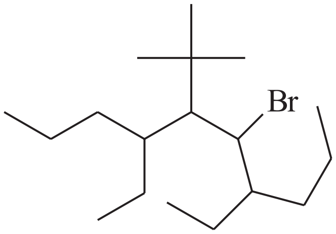
Conformational change

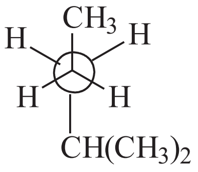
Potential energy *versus* conformational changes diagram

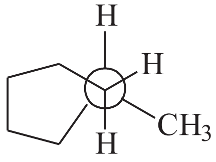
A gauche conformation with bond pair electrons and atoms far apart has lower energy and therefore higher stability than the eclipsed conformer. If two large groups attached to the Y bonds on the two adjacent C atoms are gauche to each other, the energy is increased due to steric factors affecting stability. Energy is increased even more when two large groups (R_1 and R_2) are eclipsed. Note that in addition to bond pair–bond pair repulsion and steric factors, lone pair electrons on atoms such as halogens, oxygen or nitrogen increase forces of repulsion if the two atoms bearing those lone pairs are eclipsed.

Activity

1. Draw the Newman projections of the eclipsed and staggered (gauche and anti) conformations of 1,2-dichloropropane by looking down the C(1)-C(2) bond
2. Write the IUPAC names of the following compounds:







5.8 Reactions of alkanes

Alkanes are non-polar and generally less reactive. They can however undergo halogenation (addition of halogen atoms) in the presence of light and combustion (oxidation).

5.8.1 Combustion of alkanes

Combustion of alkanes involves heating in the presence of oxygen to produce carbon dioxide, water and energy. Learners are expected to be able to balance the combustion reaction equations of alkanes. The formula C_nH_{2n+2} is very critical in this case.

Activity

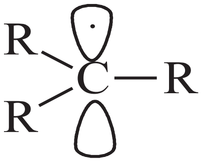
Write a balanced reaction equation for the combustion of an alkane with 6 carbon atoms.

5.8.2 Reaction Intermediates

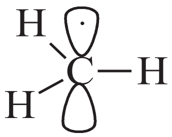
Substrates/ starting materials react to form reaction intermediates (neutral or charged) that lead to the formation of products. Reaction intermediates are like a bridge between the reactants (starting materials) and the products; the stronger the bridge the better the chances of crossing over safely to the other side. A more stable intermediate is formed preferentially and leads to preferential formation of the product. **To master reaction mechanisms requires a thorough understanding of intermediates and their relative stabilities**. At this stage we shall focus our attention on the description of the structure of free radicals and factors that affect their stability.

5.8.3 Free Radicals and Factors that Affect their Stability

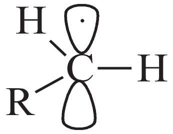
A free radical is a neutral carbon species with three bond pair electrons and a half-filled p-orbital. It runs short of a single electron to complete the octet state or noble gas configuration.



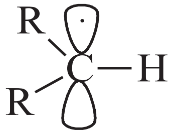
Free radicals can be classified as methyl radical, 1° radical, 2° radical or 3° free radical depending on the nature of the radical centre (electron deficient carbon). The half-filled carbon is only one electron-poor or deficient and therefore electron deficient and thus electron-withdrawing. It pulls electron density from the neighbouring carbon atoms to become less electron poor. By so doing it reduces its energy and becomes relatively more stable. The more electron donating alkyl groups are present around the radical carbon, the less electron poor it becomes. Thus a 3° free radical is less electron poor or more electron rich than the 2° radical, which in turn, is less electron poor than the 1° free radical. We say alkyl groups around a free radical carbon are electron donating (conversely, the free radical carbon is electron withdrawing because it is in need of extra electron). Note that hydrogen atom is neither electron-donating nor withdrawing and therefore the methyl radical is the least stable of them all.



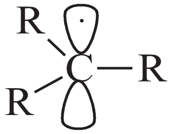
Methyl



primary (1°)



secondary (2°)



tertiary (3°) free radicals

In any chemical reactions involving formation of free radicals, if both 2° and 3° free radicals can be formed, the 3° free radical will be formed preferentially to form high proportion of the product. This is because a tertiary (3°) free radical is more stable and preferred to form than the 2° free radical.

Although we say most stable, the intermediates are still not in noble gas configuration and therefore will react upon formation to yield product(s).

5.8.4 Halogentaion of Alkanes and the Free Radical Mechanism

In the presence of heat or light, alkanes undergo halogenation to produce mixtures of halogenated products *via* a free-radical chain reaction mechanism.

Mechanism of halogenation of alkanes

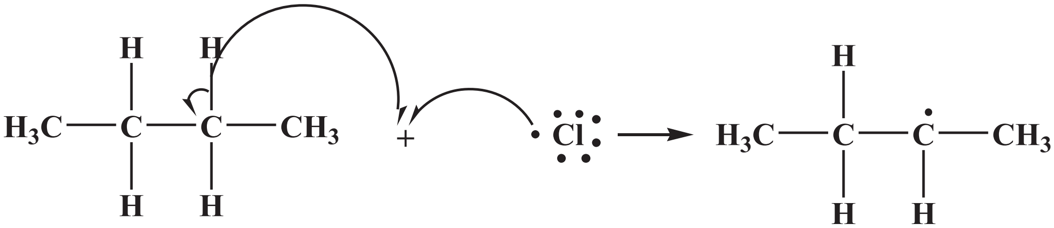
In the presence of heat and light, alkanes undergo halogenation reaction to a generate mixtures of haloalkanes or alkyl halides. The following steps represent chlorination of n-butane:

Step 1: Chain initiation step

In the presence of light, homolytic bond cleavage occurs in Cl_2 gas to form chlorine atoms.

Step 2: Chain propagation steps

(i)

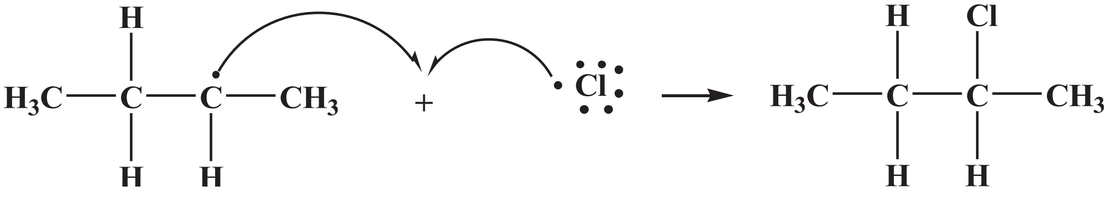


I

II

Chlorine atom abstracts a hydrogen **atom** from n-butane (I) to generate a secondary free radical (II), which is more stable than the primary radical.

(ii)

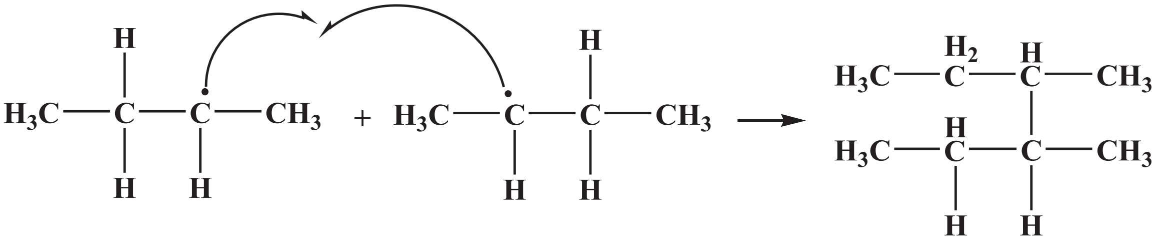


II III

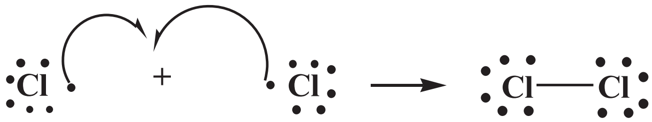
The secondary free radical (II) reacts with chlorine atom to form 2-chlorobutane (III). 1-Chlorobutane is not be formed because it forms from a less stable primary free radical

Step3: Chain termination step

In the chain termination step unreacted free radicals (from step 2) recombine to form molecules (IV and Cl_2), thereby terminating the reaction.



IV



Activity

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1. Write a balanced chemical equation for the combustion of each of the following compounds:
   (a) Methylcyclononane
   (b) Cyclodecane
2. Describe the structure of a free radical in detail.
3. Propose a detailed mechanism for the monochorination of propane and briefly

explain one isomer in preference to the other one.

Summary

You should now be able to formulate and describe physical and chemical properties of saturated hydrocarbons.

More specifically, you should be able to:

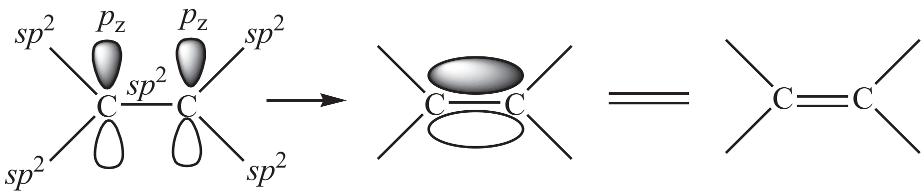
- Describe the generalized structure of alkanes and IUPAC rules for nomenclature.
- Describe the generalized structure of cycloalkanes and IUPAC rules for nomenclature.
- Explain the types of carbon atoms
- Construct various structural and conformational isomers.
- Describe reactions of alkanes.

STUDY UNIT 6

Unsaturated Hydrocarbons (Alkenes and Alkynes)

6.1 Generalized description of an alkene structure

Alkenes are unsaturated hydrocarbons characterized by a carbon-carbon double bond. Each carbon of the double bond is sp^2 hybridized and bonded to three other atoms by sigma bonds (formed through head-on overlap of the sp^2 hybrid orbitals). The remaining 2p unhybridised orbital, one on each carbon of the double bond has a lobe above and below the plane of the molecule and contain one electron each. In the unhybridized C atom, the three p orbitals are perpendicular to one another. After hybridization, the unhybridized p_z orbital is still perpendicular to the plane of the sp^2 hybrid orbital. The two unhybridised orbitals overlap sideways to form a pi bond.



Pi (π) electron cloud above and below

The geometry around the C-C double bond is flat/ planar and trigonal with bond angles of 120°. The pi bond is weaker than the sigma bond and in any chemical reaction, the pi bond is donated to the electron seeking species (electrophile). A double or half-headed arrow therefore moves from the middle of the pi bond to the electrophile (electron seeking species). Alkenes serve as sources of pi electrons and are therefore nucleophilic.

Activity

Show how C can be hybridized to sp^2 state. **Note:** label orbitals as core shell, hybridized and unhybridized.

6.2 Nomenclature of alkenes

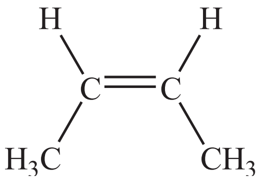
The IUPAC rules for naming alkanes are adapted in a modified way, with the longest continuous carbon chain being the one that contains the C-C double bond. The longest continuous carbon chain should be numbered in such a way that the carbon of the double bond takes the smallest whole number. The other rules are as for alkanes. The name for the longest parent alkene is modified by substituting the suffix -ane of the alkane with the same number of C atoms by the suffix -ene.

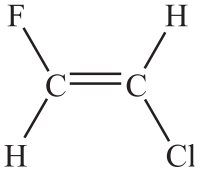
6.3 Geometric isomers

Geometric isomers are the result of the different arrangement of groups within a plane formed by the double bond. They have different physical properties, but similar chemical properties.

Di-substituted alkenes

The alkene geometry can be designated as *cis* or *trans* depending on the relative position of the large groups on the carbons forming the double bond. The designation *cis* implies groups on the same side of the carbon-carbon double bond. The designation *trans* means that the groups are on the opposite sides of the carbon-carbon double bond. It is important to draw the geometry around the C-C double bond to reflect the planar and trigonal nature as well as bond angles of 120˚.


cis


trans

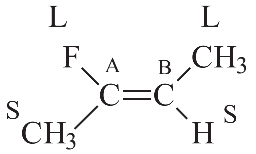
The designation *cis* and *trans* is restricted to disubstituted alkenes.

Tri- and tetra-substituted alkenes

Since the c*is* and *trans* notation is restricted to disubstituted alkenes, for tri- and tetrasubstituted alkenes we use the notation E (opposite side) and Z (same side) to designate the relative positions of large groups. Here it is again important to draw the geometry around the C-C double bond to reflect the planar and trigonal nature as well as bond angles of 120˚. Sequence rules have been designed to designate E and Z stereochemistry.

Sequence Rules for E and Z notation

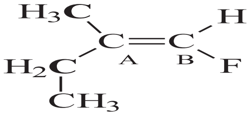
(i) Compare the priorities (atomic number) of the two atoms **directly** bonded to each carbon of the double bond. The one with higher priority is labeled large (L) and the other small (s). If the two large groups are on the same side of the carbon-carbon double bond the geometry becomes Z.



On C_A, F > C On C_B, C > H

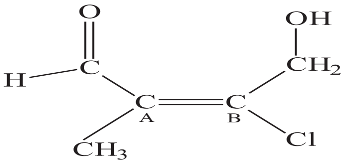
The designation is Z geometry

(ii) Should the two atoms **directly** bonded to each carbon of the C-C double bond be similar, move further until a point of difference is obtained.



On C_B, F > H. On the other hand, for C_A, both methyl and ethyl groups are attached by **C**. The difference between the two is that the methyl group has H which is smaller than the second C of the ethyl group. As a result, $CH_3CH_2 > CH_3$. The designation is Z geometry with F and CH_3CH_2 on the same side of the double bond

(iii) For multiple bonded groups (double or triple) each atom of the multiple bond is multiplied according to the multiplicity of the bond (2 for double and 3 for triple bond)



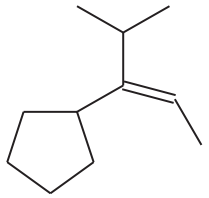
C_A: H+2xO+2x C > CH_3 C_B: Cl > C

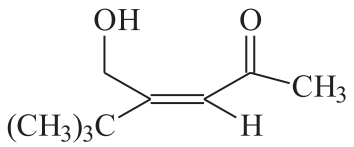
The designation is E geometry.

It is important to understand these sequence rules as they will be extended and applied to stereoisomers (enatiomers) at a later stage.

Activity

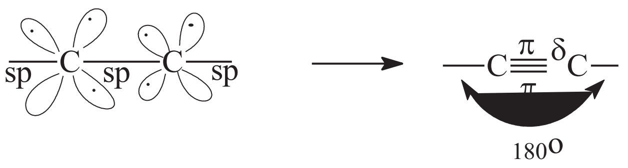
(i) For each structure below assign priorities to the substituents and then provide the appropriate E or Z stereochemistry designator:





6.4 Generalized Description of an Alkyne Structure

Alkynes are characterized by a carbon-carbon triple bond and each carbon of the triple bond is sp hybridized and bonded to two other atoms by sigma bond formed using sp hybrid orbital. The remaining unhybridized p_y and p_z orbitals overlap side ways to form two pi bonds. The geometry around the triple bond is linear with bond angle of 180˚.



The triple bond is made up of one sigma bond (**middle**) and two pi bonds one above and the other below the sigma bond. Alkynes are also sources of pi electrons (nucleophiles) and can donate in sequence one pair of pi electrons to change from triple to double and another pair to a single bond state, respectively.

Activity

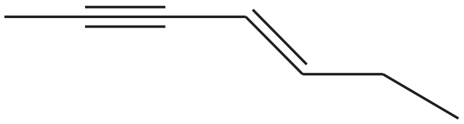
Show how C can be hybridized to sp state. **Note:** label orbitals as core shell, hybridized and unhybridized.

6.5 Naming of Alkynes

The systematic name of an alkyne is obtained by replacing the “ane” ending of the alkane name with the “yne”. The longest continuous chain containing the carbon – carbon triple bond is numbered in the direction that gives the alkyne functional group suffix the lowest possible number.

What about an unsaturated molecule that contains both double and triple bonds?

If several multiple bonds are present, each must be assigned a locator number. Double bonds precede triple bonds in the IUPAC name, but the chain is numbered from the end nearest a multiple bond, regardless of its nature



3-Hepten-5-yne

Activity

Draw the structure of each of the following compounds

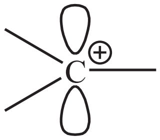
a) 1-Chloro-3-hexyne

b) 4-bromo-2-pentyne

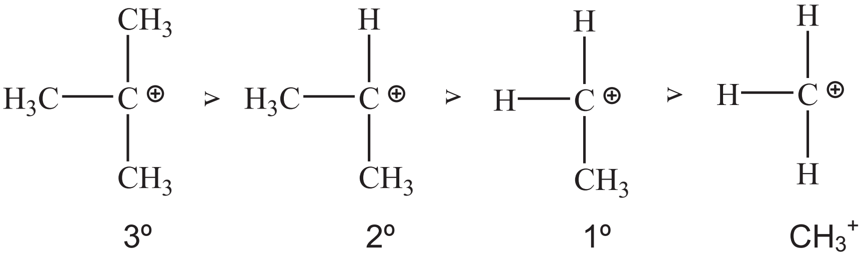
c) 4,4-dimethyl-1-pentyne

6.6 Carbocations and Factors that Affect their Stability

A carbocation is a positively charged carbon species in which the carbon atom has three bond pair electrons and runs short of a pair of electrons to complete the noble gas (octet state) configuration in order to resemble neon. The positively charged carbon is electron poor (deficient) and will accept a pair of electrons from a nucleophile. A carbocation centre (positively charged carbon) has an empty p orbital with two lobes shaped like a figure **8** above and below the plane of the carbon framework. It is this orbital that accepts a pair of electrons from the nucleophile.



The types of carbocations include methyl carbocation (CH_3^+), 1° carbocation (RCH_2^+), 2° carbocation (R_2CH^+) and 3° carbocation (R_3C^+). The positively charged carbon is electron poor and therefore strongly electron-withdrawing. It pulls electrons from the neighbouring carbon atoms to become less positive and therefore less electron poor. By so doing it reduces its energy and become relatively more stable. The more electron donating alkyl groups there are around the positively charged carbon, the less positive it becomes. A 3° carbocation is thus less positive than the 2° carbocation which in turn is less positive than the 1° carbocation. The hydrogen atom is neither electron-donating nor withdrawing and therefore the methyl carbocation is the least stable.



Trend in stability of carbocations: 3° > 2° > 1° > CH_3^+

If both 2º and 3º carbocations were to be formed from the same unsymmetrical alkene, the 3º carbocation, which is more stable will be formed preferentially and will yield a high proportion of the product.

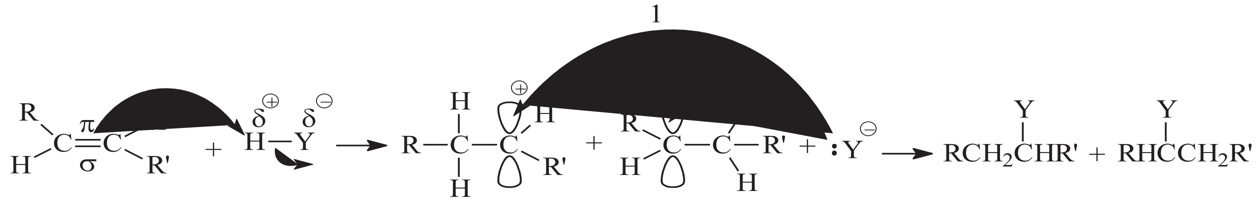
6.7 Reactions of Alkenes and Alkynes

Alkenes and alkynes are sources of pi electrons (nucleophiles) and they both undergo electrophilic addition. The reactivity of alkenes and alkynes and the proportion and type of the addition products formed depend on the structure of the unsaturated hydrocarbon molecule. The latter can be classified as either symmetrical or unsymmetrical, based on the plane of symmetry, which bisects the double or triple bond. If one cuts through the middle of a double or triple bond and the two halves are similar or equivalent then the molecule is symmetrical. For unsymmetrical alkenes and alkynes, the two halves are unequal and therefore different.

In any electrophilic addition reaction to an alkene or alkyne, the pi bond electrons are always the ones that attack the electron poor species (electrophile). Since the pi electrons are equally shared by both carbon atoms of the double or triple bond, anyone of the carbon atoms of the double or triple bond can use the pi bond electrons independently to attach the electrophile. For unsymmetrical alkenes and alkynes, the preferred addition will depend on the stability of the carbocation which is formed. The relatively more stable carbocation is formed preferentially and it in turn reacts faster to form the product in relatively large amount. Thus, if a mixture of products is formed, both carbocations have to be included in the mechanism and their relative stabilities compared. If only one product is formed, this implies that only the most stable carbocation is produced to form the product, i.e., it is the sole/ only product.

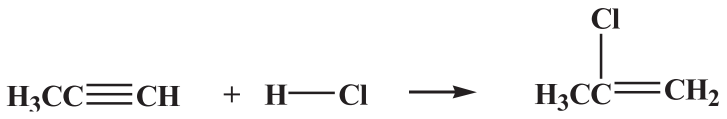
6.7.1 Electrophilic addition to alkenes and alkynes

The pi electrons always attack an electron-poor species to form carbocation(s). In the example below, if R = R' the alkene is symmetrical and therefore the two carbocations formed will be similar and will therefore form the same product. On the other hand, for unsymmetrical alkenes R ≠ R' and thus a mixture of carbocations may be formed. The relative stabilities of resulting carbocations will influence the proportion of the products formed. The more stable carbocation is formed preferentially, that is, it is the one that will form first and then react with the nucleophile in the second step to form the final product. A carbocation is electrophilic and runs short of two electrons (electron pair) to complete the noble gas configuration. It is thus attacked by the nucleophile (Y^-) in the second step to form either one or two products depending on the relative stabilities of the carbocations. The mechanism below is representative for HX (X = halogen), H-OSO_3H (Y = OSO_3H), H-O^+H_2 (Y = $^+OH_2$ as in the hydronium ion), etc.



In any electrophilic addition to the carbon-carbon double bond of an unsymmetrical alkene, the electrophilic hydrogen (proton) attaches to the carbon of the double bond with the most hydrogen atoms to form a more stable carbocation that results in the formation of a major or sole product (**Markovnikov's rule**).

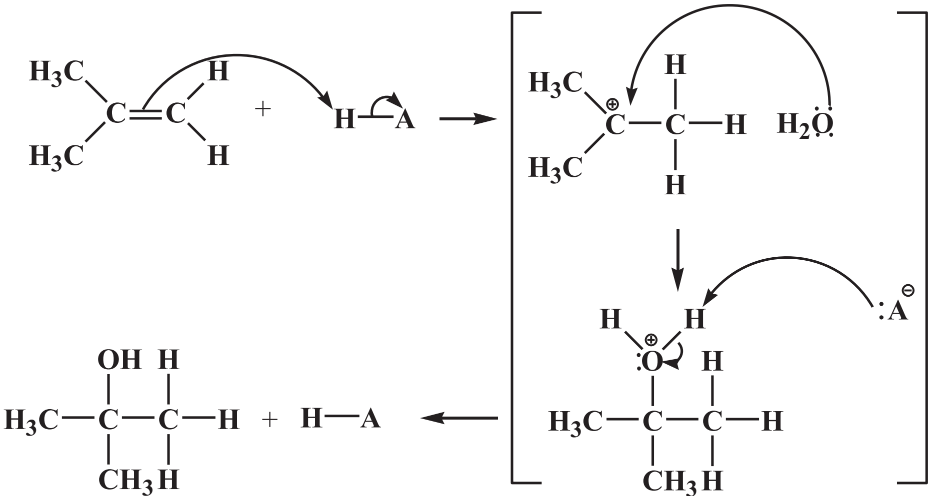
Alkynes, like alkenes, undergo electrophilic addition reactions. Note that the same electrophilic reagents that add to alkenes also add to alkynes to give alkene products.



$$H_3CC{\equiv}CH + H{-}Cl \longrightarrow H_3C\overset{Cl}{\overset{|}{C}}{=}CH_2$$

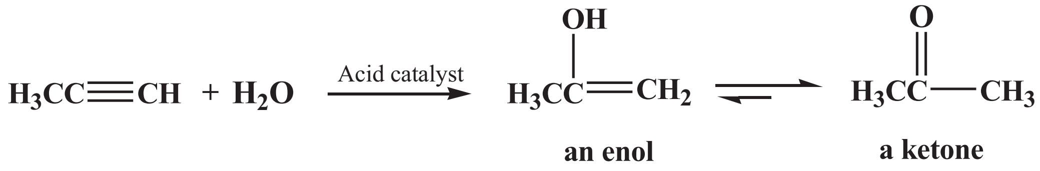
6.7.2 Acid catalyzed hydration of alkenes

In the presence of catalytic amounts of acid, water adds to simple alkenes to yield alcohols in a mechanism similar to that of H-Y addition above. Note that a catalyst kick-starts the reaction, speeds it up and is regenerated at the end of the reaction. Thus an acid or proton (H^+) is attached by the pi bond electrons of an alkene to generate a carbocation. Either carbon of the double bond can attack the proton, however, it is the formation of the more stable carbocation that directs the forward reaction. The carbocation is then attacked by oxygen of water since it bears lone pair electrons and is therefore nucleophilic. This attack leads to the formation of a protonated alcohol (ROH_2^+). The latter then loses a proton (H^+) to yield a neutral alcohol. It is at this stage where the acid catalyst is regenerated.



6.7.3 Hydration of alkynes

Alkynes also undergo acid catalyzed hydration following Markovnikov's rule with H attached to carbon bearing more hydrogens. The initial product of the reaction is an **enol** (*ene* + *ol*). An enol has a carbon-carbon double bond and an OH group bonded to one of the sp^2 carbons. The enol immediately rearranges to a **ketone** by a process called *keto-enol tautomerism.*

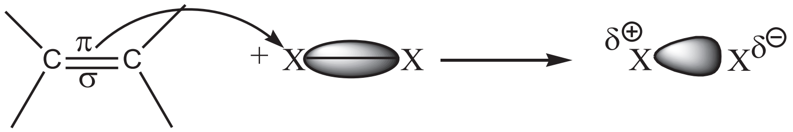


6.8 Halogenation of alkenes and alkynes

A halogen molecule (F_2, Cl_2, Br_2, I_2) is made up of two atoms of equal electronegativity and is therefore nonpolar with a plane of symmetry cutting through the sigma bond. A halogen molecule is shaped uniformly like a rugby ball.

When the pi electrons from the carbon-carbon double bond of an alkene or alkyne approach one end of the symmetrical halogen molecule, they push the electron density away (repulsion) to the other end of the halogen atom. The electron density becomes concentrated on the far end of the halogen molecule opposite to the approaching pi electrons leading to a pear or egg-like shape. The end of the halogen molecule which the pi electrons approach, becomes electron poor and therefore partially/ slightly positive (δ^+). The electron density becomes concentrated on the other end of the halogen molecule far away from the approaching pi electrons and this site becomes electron-rich and therefore slightly negative (δ^-). The C-C pi electrons therefore generally polarize a halogen molecule.

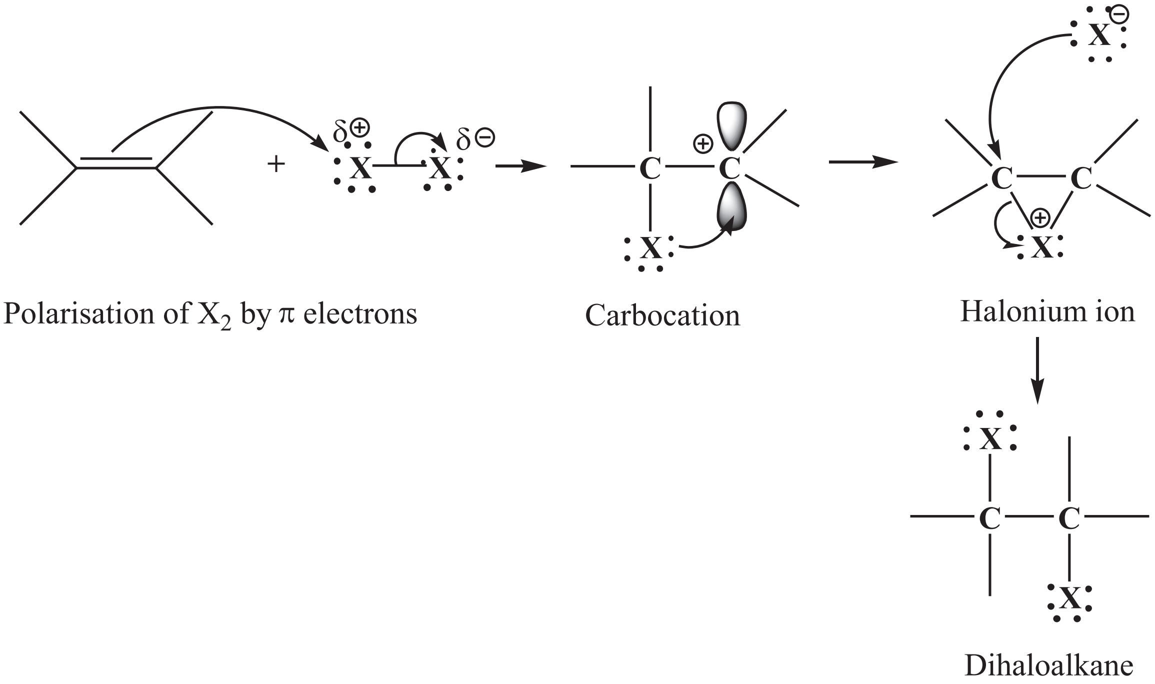
How carbon-carbon pi electrons polarize a halogen molecule.



Generalized mechanism of halogenations of alkenes

Pi electrons of an alkene attack the partially positive end of the halogen molecule resulting in bond formation between C and X and bond breakage between halogen atoms with the release of a halide ion (X^-) to form a carbocation. The electron poor carbocation has an empty p orbital with a lobe lying parallel to the adjacent electron rich halogen atom. A pair of electrons from the bonded halogen atom attacks the adjacent empty p orbital which lies parallel to X to form a positively charged halonium ion. It is important to note that in the halonium ion all atoms, including the positively charged X, are in noble gas configuration. The halonium ion is therefore more stable than the carbocation from which it is derived.

The positively charged X in the halonium ion is highly electron withdrawing and renders both carbons highly electron deficient. The negatively charged halide ion which was released in the first step then attacks the electron poor carbon on the opposite side of the positively charged halogen atom in order to avoid electron-electron repulsion between the approaching and departing electron pair. The attack leads to the formation of a dihaloalkane product with halogen atoms on opposite side of the carbon framework.



For unsymmetrical alkenes, the attack on the halonium ion will be different and may depend on steric (crowding) and/ or electronic factors (attack of more stable carbocation). Halogenation of alkenes is usually performed in a neutral or nonpolar solvent like carbon tetrachloride (CCl_4) which cannot serve as nucleophile and the halide ion reacts with the halonium ion. The situation changes when halogenations are conducted in a polar solvent that has a nucleophilic centre.

When halogenation is carried out in nucleophilic solvents such as water, alcohol or amines, the nucleophilic solvent outcompetes the halide ion released from X_2 in the second step. The solvent attacks the electron poor carbon of the halonium ion to form a product bearing a halogen atom and part of the solvent molecule.

Halogenation of alkynes

The mechanism of halogenation of alkynes is similar to that of the alkenes. However, in the case of alkynes, the use of one equivalent of halogen molecule leads to a dihaloalkene. On the other hand, the use of two mole equivalent of the halogen molecule will lead to a tetrahalogenated alkane derivative.

Activity

---

1. 1-Methyl-1-cyclohexene **A** reacts with hydronium ion to afford the two products **B** and **C** in the ratio 80:20. Propose a detailed mechanism for this reaction and provide the IUPAC names of products **B** and **C**.

2. Propose a detailed mechanism for the reaction of 2-butene with aqueous bromine and provide the IUPAC name(s) of the resulting product(s).

3. Propose a detailed mechanism for the reaction of 2-butyne with bromine (one equiv.) followed by addition of hydrogen chloride and provide the IUPAC name(s) of the resulting product(s).

6.9 Hydrogenation of alkenes in the presence of peroxide and light (anti-Markovnikov addition)

In the presence of peroxide (ROOR'; R, R' = H or alkyl) and light, hydrohalogenation of alkenes is found to afford an alkyl halide product with a hydrogen atom attached to the carbon of the double bond that previously had the least number of hydrogen atoms (anti-Markovnikov). This observation implies that a different mechanism to that of hydrohalogenation of alkenes in the absence of peroxide is under operation.

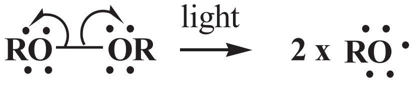
In the presence of peroxide and light the mechanism involves free radicals and not carbocations. The more stable free radical is the one that forms the product preferentially.

Generalized mechanism of hydrohalogenation of alkenes in the presence of peroxide

Step 1 Chain initiating step

In the presence of light, the peroxide (I) undergoes homolytic bond cleavage to generate the hydroxyl (if R = H) or alkoxy (R = alkyl) radicals (II).

(i)



I II

Homolytic bond cleavage of the peroxide forms free radicals. This reaction is initiated by light.

(ii)

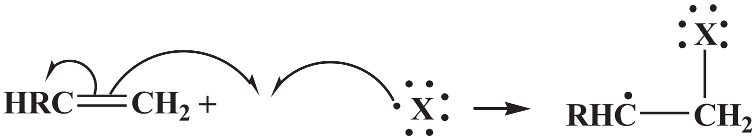
II III IV

Generation of water/ alcohol and halogen atom

The radical (II) generated above abstracts hydrogen atom from HX to form water or an alcohol (III) and a halogen atom (IV).

Step 2 Chain propagation steps

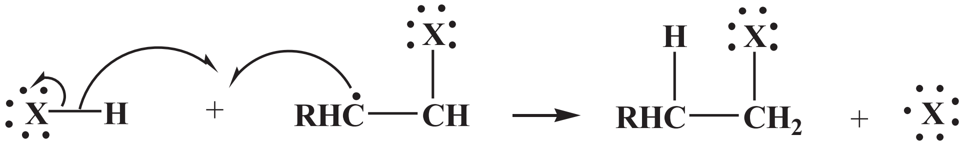
(i)



V IV VI

Halogen radical or atom (IV) released above pairs its spin with one of the pi electrons from the C-C double bond of an alkene (V) to form a bond. The other pi electron is taken by the second carbon of the double bond to generate a more stable free radical (intermediate VI). For unsymmetrical alkenes, formation of a more stable free radical is preferred (*recall factors that affect the stability of free radicals*).

(ii)

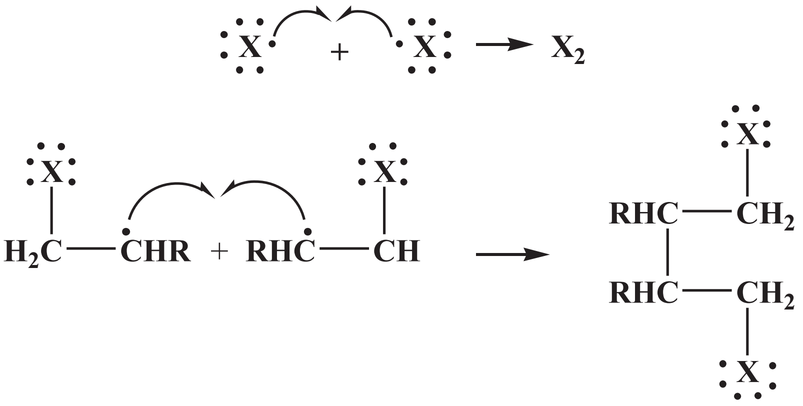


VI **VII** **IV**

The halogenated free radical (VI) abstracts a hydrogen atom from excess H-X to form an alkyl halide (VII) releasing a halogen atom (IV). In the product (VII), the hydrogen atom is attached to the carbon of the double bond with the least number of hydrogen atoms (anti-Markovnikov fashion).

Step 3 Chain Terminating Steps

This step involves a random recombination of free radicals generated in steps 2 and it stops when there are no more radicals in the mixture.



Activity

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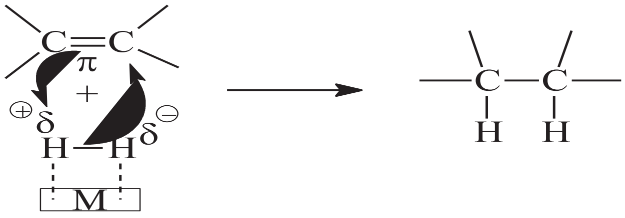
1. Propose a detailed mechanism for the reaction of propene with hydrogen bromide in the presence of hydrogen peroxide.
2. Peroxide-free hydrobromination of propene affords a sole product in 100% yield. Propose a mechanism for this reaction.

6.10 Hydrogenation of alkenes and alkynes

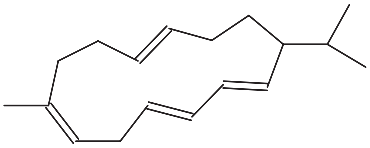
Hydrogenation (also known as reduction) involves addition of hydrogen atoms from a hydrogen molecule to the alkene double bond. The reaction occurs on the surface of a metal catalyst (Pd, Ni or Pt). The nonpolar hydrogen molecule is adsorbed onto the metal surface and becomes polarized. The mechanism of hydrogenation of the carbon-carbon pi bond occurs in one step in a concerted fashion. The hydrogen atoms are added on the same face/side of the C-C double bond.



Alkynes also undergo hydrogenation, however, in this case the functionality of the resulting product depends on the amount or proportion of the hydrogen molecule used. One mole equivalent of hydrogen reduces an alkyne to an alkene and the second equivalent of H_2 will completely reduce the resulting alkene to and alkane. *The application of precious metals such as nickel, palladium and platinum in synthetic organic chemistry is referred to as beneficiation.*

Activity

Cembrene shown below is a component of pine oil:



(a) How many moles of hydrogen gas will completely hydrogenate cembrene?

(b) What is the molecular formula of the saturated hydrocarbon in (a)?

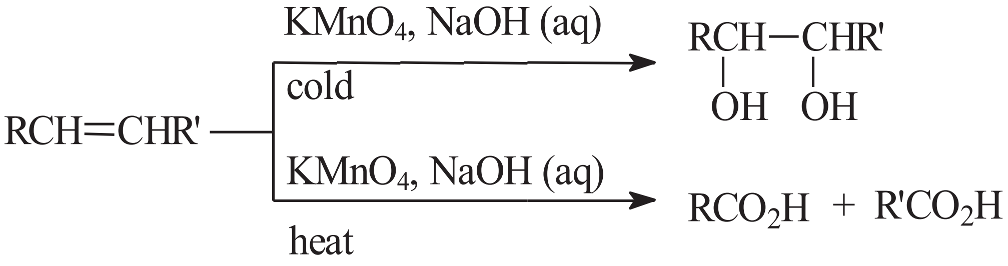
(c) Write a balanced reaction equation including the physical states of the reactants and products of combustion of the product in (b).

6.11 Oxidation of alkenes

Alkenes undergo hydroxylation in the presence of potassium permanganate to afford either the diols or carboxylic acid derivatives. They also react with ozone to afford ketones and/ or aldehydes.

6.11.1 Hydroxylation of alkenes

Cold alkaline aqueous potassium permanganate solution adds to the C-C double bond to afford 1,2-diol derivative with the release of MnO_2 as a by-product. On the other hand, hot alkaline $KMnO_4$ cleaves the C-C double bond to form carboxylic acid derivatives. A terminal $=CH_2$ group is always completely oxidized to carbon dioxide.



The mechanisms of these reactions are not important at this stage, however, learners are expected to be able to predict, draw and name the structures of the products of hydroxylation reactions.

Activity

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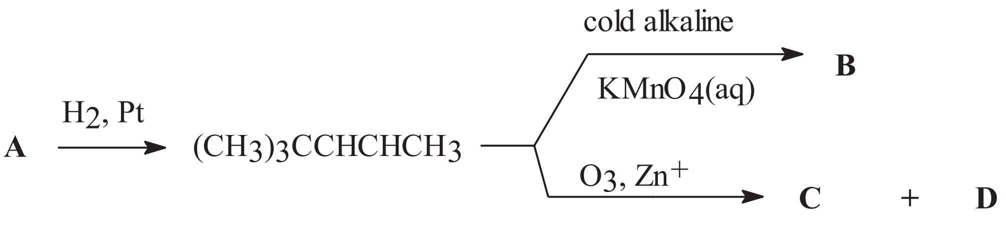
1. The following scheme is incomplete:



(a) Write the structure and the IUPAC name of compound **A**.

(b) Write the structure and the IUPAC name of product **B**.

(c) Write the structures and the IUPAC names of products **C** and **D**.

2. Draw the structures corresponding to the missing products in the following reactions:

(a) 2-Methyl-2-pentene + cold alkaline $KMnO_4$ (aq) →

(b) 2-Butene + $KMnO_4$ (hot) →

6.11.2 Ozonolysis of Alkenes

Ozonolysis of alkenes proceeds through an ozonide intermediate to form carbonyl derivatives. Symmetrical alkenes will form the same product, whereas unsymmetrical alkenes yield mixtures of carbonyl compounds. Dimethyl sulfoxide (DMSO) is always released as a by-product.

Activity

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1. Draw the structures of the product(s) of the ozonolysis of each of the following compounds:

(a) 3-Ethyl-2-pentene;

(b) 2-Ethyl-3-methyl-2-pentene

2. Draw the structures corresponding to the missing products.

(a) Cyclohexene + ozone + $(CH_3)_2S$ →

6.12 Interconversion of Alkynes, Alkenes and Alkanes

Alkenes, alkanes and alkynes can be interconverted using various reagents and reaction conditions. Learners are expected to use their knowledge of reaction mechanisms to interconvert alkanes, alkens and alkynes

<u>Summary</u>

You should now be able to formulate and describe physical and chemical properties of unsaturated hydrocarbons (alkenes and alkynes).

More specifically, you should be able to:

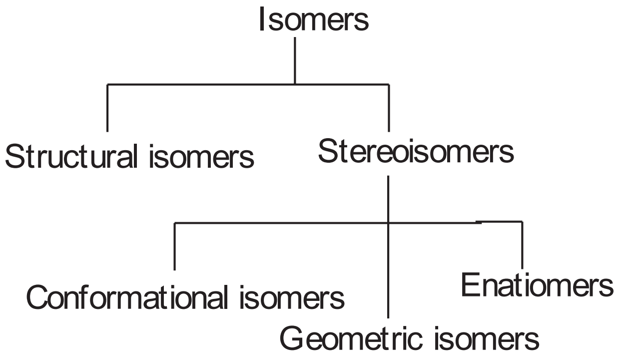
- Describe generalized structure of alkenes and nomenclature.
- Describe generalized structure of alkynes and nomenclature.
- Describe reactions of unsaturated hydrocarbons.
- Treat mechanisms of hydrohalogenation, hydration, halogenations of symmetrical and unsymmetrical alkenes and alkynes and the application of Markovnikov's rules in relation to carbocation stability.
- Formulate mechanisms of hydrohalogenation of alkenes in the presence of light and compare the stability of free radicals.
- Develop strategies for the inter-conversion of alkynes, alkenes and alkynes using various reagents.

STUDY UNIT 7

Introduction to Stereochemistry

7.1 Isomers and their classification

Isomers are compounds with the same molecular formula (composition) but different structural formulas. There are several types of isomers and these are summarized below:



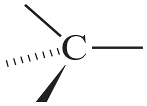
Structural, conformational and geometric isomers were discussed before under alkanes and alkenes. In this section we shall focus mainly on enantiomers.

7.2 Enantiomers

These are stereoisomers in which the molecules are non-superimposable mirror images of each other. The most common situation occurs when a tetrahedral carbon (sp^3 hybridized) is attached to four different atoms or groups of atoms. The resulting molecules have no plane of symmetry and are therefore asymmetric.

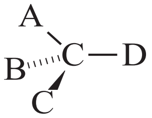
7.3 Three-Dimensional Structure of a Tetrahedral Carbon

This requires a tetrahedral carbon to be drawn as a 3-dimensional structure with a wedged solid bond facing the viewer and the broken line representing the bond away on the opposite side of the observer, while the remaining two bonds are in the plane of the paper.



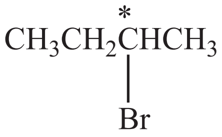
7.4 Chirality and Stereoisomers

Your right and left hands are very similar, yet they are not identical. They are related to each other as **mirror images**, and as such they cannot be superimposed on top of each other. This is known as chirality. Molecules can also be chiral if they contain one or more **chiral centers**. For the purposes of introductory organic chemistry, a chiral carbon also known as stereogenic centre, is sp^3 hydridized carbon atom that is bonded to four different atoms or substituents, A # B # C # D, and is usually designated by an asterisk (*). The arrangement in space of atoms about a chiral carbon is represented by the following configuration:

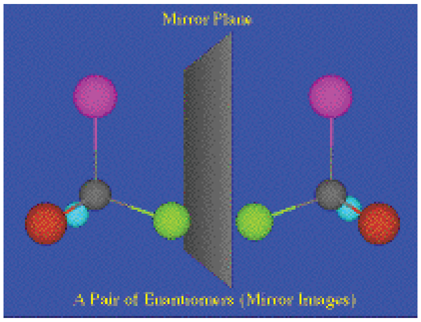


A more contemporary term for "chiral center" (or chiral carbon) is **stereogenic center** (or stereocenter), and the terms will be used interchangeably. The following structures will clarify this principle:

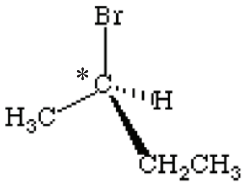
2-Bromobutane



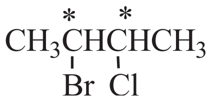
$$\mathrm{CH_3CH_2\underset{\displaystyle Br}{\overset{*}{C}}HCH_3}$$



In 2-bromobutane the carbon (carbon-2) to which bromine is bonded is a stereogenic center; it is sp^3 hydridized and it is bonded to four different groups: hydrogen, bromine, methyl group, and ethyl group. All of the other carbons in this molecule are **not** stereogenic centers, since they are all bonded to at least two similar atoms, in this case hydrogens.



2-Bromo-3-chlorobutane



$$\mathrm{CH_3\underset{\displaystyle Br}{\overset{*}{C}}H\underset{\displaystyle Cl}{\overset{*}{C}}HCH_3}$$

2-Bromo-3-chlorobutane has two stereogenic centers. Carbon-2 in this molecule is sp^3 hydridized and is attached to four different groups: H, Br, CH_3 and $-CHClCH_3$. Likewise, carbon-3 is also sp^3 hydridized and is attached to four different groups: H, Cl, CH_3 and $-CHBrCH_3$.

According to the Van't Hoff 2^n rule, a compound with n chiral or asymmetric carbon atoms often has 2^n stereoisomers. Therefore 2-bromobutane is expected to have $2^1 = 2$ stereosiomers, and 2-bromo-3-chlorobutane has $2^2 = 4$ stereosiomers.

Steps to be Followed in the Assignments of R or S Configurations

The configuration of a chiral carbon can be defined as R (clockwise or rotation to the right) or S (anticlockwise or rotation to the left). The following steps must be followed to assign R or S configurations:

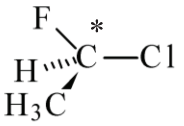
- Identify the chiral centre and mark it with a small asterisk (*)
- Arrange the **atoms** or groups around the chiral center according to priorities (atomic number). The highest priority element is given number 1 and so on to the lowest priority atom which receives priority number 4.
- The arrangement of groups of atoms (substituents) about the chiral center follows the sequence rules similar to those previously applied for the assignment of **E** and **Z** geometry (**revisit sequence rules under alkenes**). The only difference is that in this case we compare the four substituents around the chiral carbon together.
- Now view the molecule through the chiral center–lowest priority bond (C*–4).
  The lowest priority atom or group should always be away on the opposite side of the viewer. A clockwise rotation from the highest priority (1) through the second priority (2) to the third priority and back to first priority (1) is designated R-configuration. An anti-clockwise rotation from the highest priority (1) through

the second priority (2) to third priority and back to first priority (1) is designated S-configuration.

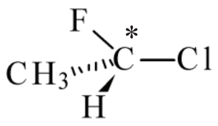
Note that if given the molecule with the lowest priority atom or group away from the observer, the rotation obtained is as it is. On the other hand, if the lowest priority group is closer or on the same side as the observer then the rotation is the opposite of what we obtain if the whole molecule is not rotated.

- For molecules with two chiral centers, perform the rotation per chiral centre with the other chiral carbon being a substituent to the centre under attention.

Let us assign R or S- configuration to molecules **A** and **B** below. In both molecules there is a single chiral carbon at the center. Trend in atomic numbers/ priorities: Cl > F > C > H which implies that Cl (1), F (2), C (3) and H (4).



A



B

For molecule **A**, the lowest priority atom (H) is far away from the observer and when we rotate from Cl to F (in the plane) then to CH_3 and back to Cl we go in an anticlockwise direction on page, then the configuration is S.

For molecule **B** the lowest priority group (H) is closer to the observer. In this case, imagine yourself standing on the opposite side of H (between F and Cl) looking at the chiral carbon–lowest priority bond (C–H). Rotate from Cl to F then to CH_3 and back to Cl. Although the rotation on paper goes in an anticlockwise direction, because you are standing on the opposite side then the actual rotation is clockwise relative to you being on the other side. Therefore we have a R configuration in B.

Activity

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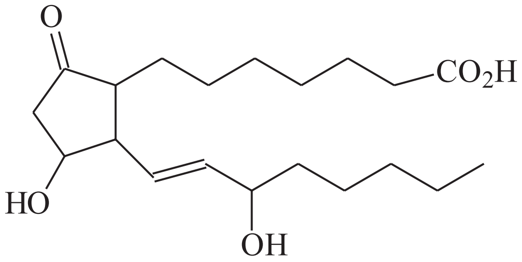
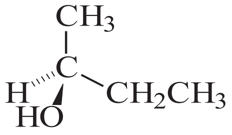
1. The structure of prostaglandin E_1 is shown below:

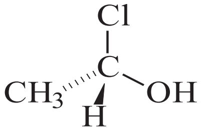


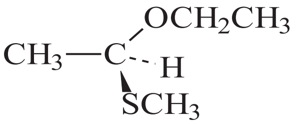
(a) Indicate each chiral centre in the above molecules with an asterisk (*).

(b) How many possible stereoisomers of prostaglandin E_1 exists? Motivate your answer.

2. Follow the sequence rules to assign R or S configuration to each stereogenic center of the following compounds:







Summary

You should now be able to formulate and describe various stereoisomers.

More specifically, you should be able to:

- Name structural and constitutional isomers are constructed from molecular formulae.
- Construct geometric isomers and compare their stabilities.
- Construct the 3-dimensional structure of carbon.
- Apply rules for assigning R or S configurations to chiral carbons.

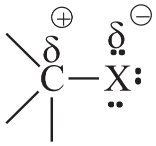
STUDY UNIT 8

Alkyl Halides

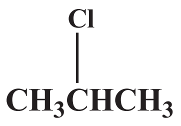
8.1 Generalized description of alkyl halides
8.2 Preparation and classification of alkyl halides
8.3 Reactions of alkyl halides (nucleophilic substitution reactions)
8.4 Elimination reactions (E1 *versus* E2)

8.1 Generalized description of alkyl halides

Alkyl halides are characterized by an sp^3 hybridized carbon bonded to a halogen atom (X = F, Cl, Br, I). The high electronegativity of the halogen atom causes X to draw the C-X bond pair electron density towards itself leaving the carbon to which X is bonded electron poor and therefore partially positive. The halogen atom becomes electron rich and therefore slightly negative. The C-X bond is thus polar with the dipole moment moving from C to X. In any chemical reaction when the C-X bond breaks, the halogen atom takes both bond pair electrons, leaving the carbon to which X is bonded electron poor and therefore susceptible to nucleophilic attack.

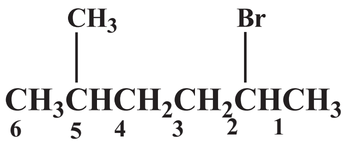


In the IUPAC system, alkyl halides are named as substituted alkanes. The substituent prefix names for the halogens end with “o” (i.e., “fluoro”, “chloro”, “bromo”, “iodo”)



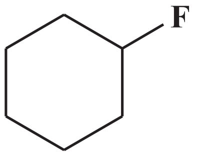
$CH_3\underset{}{\overset{Cl}{C}}HCH_3$

2-chloropropane



$\underset{6}{CH_3}\underset{5}{\overset{CH_3}{C}H}\underset{4}{C}H_2\underset{3}{C}H_2\underset{2}{\overset{Br}{C}H}\underset{1}{CH_3}$

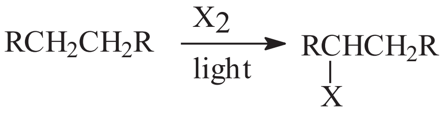
2-bromo-5-methylhexane



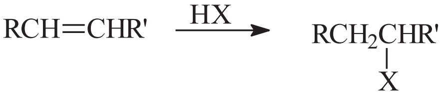
fluorocyclohexane

8.2 Preparation and classification of alkyl halides

Alkyl halides can be prepared from alkanes by halogenation in the presence of peroxide and light. They can also be prepared through hydrohalogenation and halogenation of alkenes and alkynes. Learners are required to revisit some of the reactions treated before for the mechanisms:



$$RCH_2CH_2R \xrightarrow[\text{light}]{X_2} R\underset{X}{C}HCH_2R$$



$$RCH{=}CHR' \xrightarrow{HX} RCH_2\underset{X}{C}HR'$$

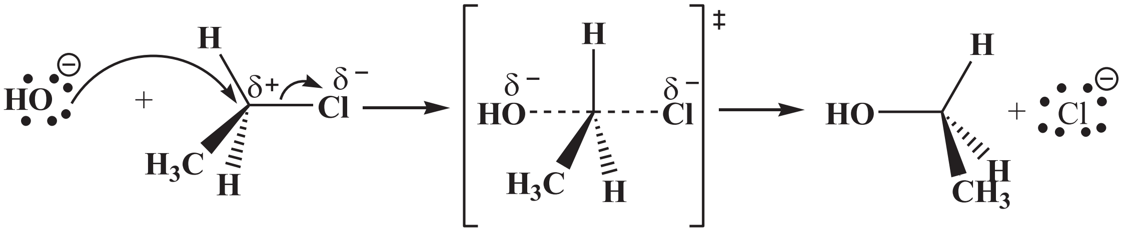
The preparation of alkyl halides from alcohols through nucleophilic substitution will be discussed later.

Alkyl halides are classified as *primary, secondary,* or *tertiary,* depending on the carbon to which the halogen is attached. Primary alkyl halides have the halogen attached to a primary carbon, secondary alkyl halides have the halogen attached to a secondary carbon, and tertiary alkyl halides have the halogen attached to a tertiary carbon. They can undergo nucleophilic substitution reactions to form alcohols, ethers, amines, *etc*. In substitution reactions, the electronegative atom or electron-withdrawing group (X = F, Cl, Br, I) is replaced by another atom or group. Alkyl halides can also undergo elimination reactions to form alkene product(s). In an elimination reaction, the electronegative atom or electron-withdrawing group (X = F, Cl, Br, I) is eliminated, along with a hydrogen from an adjacent carbon. The atom or group that is substituted or eliminated in these reactions is called a leaving group.

8.3 Reactions of alkyl halides (nucleophilic substitution reactions)

8.3.1 S_N2 reaction of alkyl halides

In an S_N2 mechanism, the nucleophile approaches the electrophilic carbon at an angle of 180° on the opposite side of the leaving group. The reaction proceeds *via* a transition state where both bond formation and bond breakage occur simultaneously. N**o intermediate** (carbocation or free radical) is formed. In the transition state, the tetravalent carbon becomes somewhat pentavalent with 50% bond formation and 50% bond breakage. The mechanism is restricted to **all** primary alkyl halides and most of the secondary alkyl halides. This is because bond breakage between C and X (X = F, Cl, Br, I) will result in relatively less stable primary or secondary carbocations. Due to bond pair–lone pair repulsion (recall VSEPR theory) the geometry/ stereochemistry becomes **inverted** with the nucleophile occupying the opposite side to that previously occupied by the leaving group. Like an umbrella on a windy day, the other three bonds which were there shift towards the side of the leaving group to reduce bond pair–lone pair repulsion.



tetravalent carbon

pentavalent carbon
Transition state with
partial bond formation
between C and O and partial
bond breakage between C and Cl.

In the transition state, oxygen becomes partially (50%) negative and at the same time a partially negative charge (50%) develops on Cl. In the above example the alkyl halide has no chiral centre and therefore no R or S configuration.

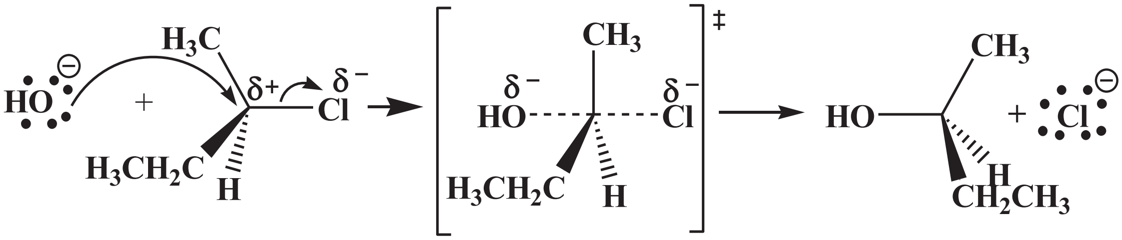
The rate of S_N2 reactions depends on both the concentration of the nucleophile and the electrophile (RX) and is expressed as follows:

$$R = k[HO^-][RCl]$$

No reaction can take place without the nucleophile approaching the electrophile.

S_N2 mechanism for chiral secondary alkyl halides and inversion of configuration

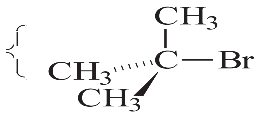
S_N2 requires reverse-side attack of the electrophilic carbon of the tetravalent molecule and it occurs at 180˚ on the opposite site of the leaving group.



R-configuration S-configuration

Why can tertiary alkyl halides not undergo S_N2 reaction?

For the tertiary alkyl halides, the reverse side is sterically hindered by the bulky groups preventing access by the nucleophile. Furthermore, S_N2 involves a pentavalent transition state which would be highly crowded and less favoured in the case of tertiary alkyl halides.



Highly crowded side

Alkyl groups prevent the nucleophile from accessing the electrophilic C.

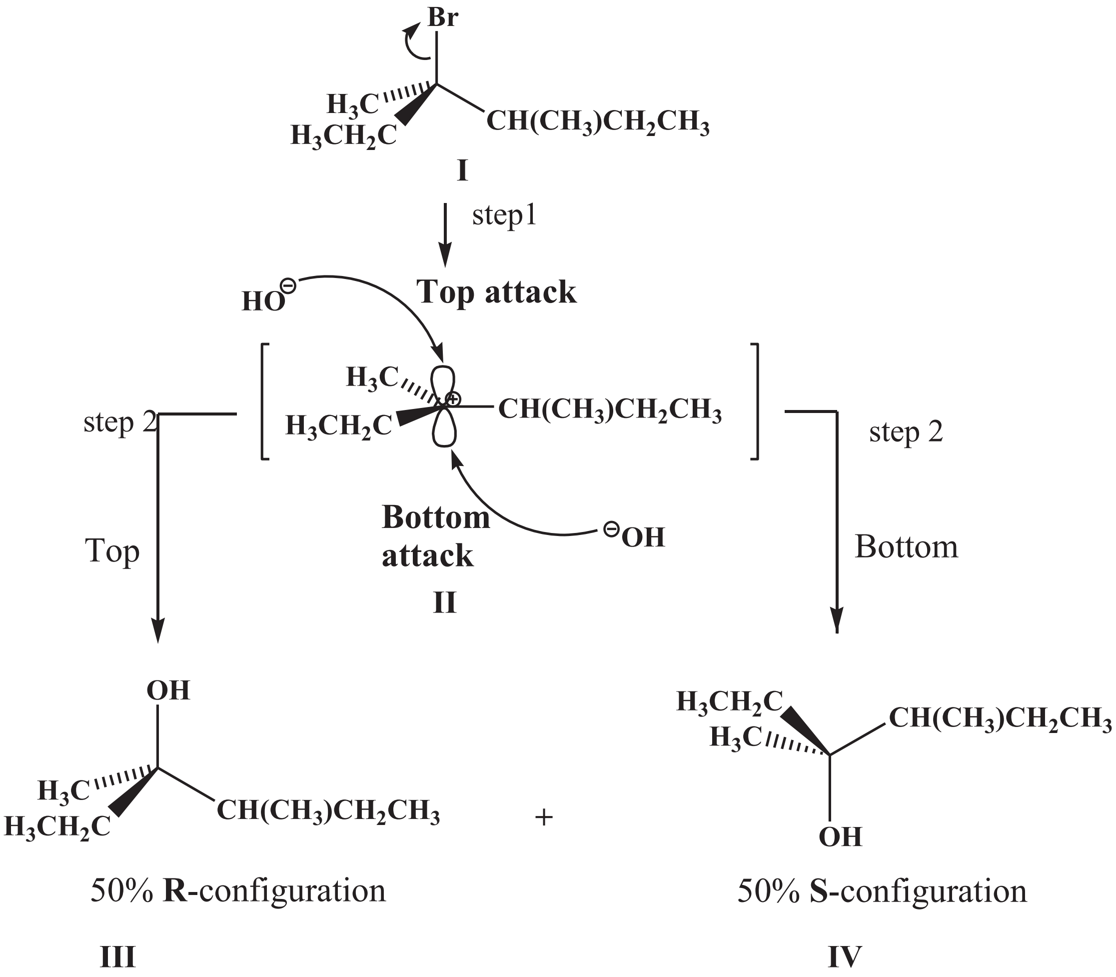
8.3.2 S_N1 Reaction of Alkyl Halides

The S_N1 mechanism is restricted to tertiary alkyl halides which are sterically hindered for reverse-side attack by the nucleophile. The driving force for this reaction is the formation of a **more stable tertiary carbocation**, which is trivalent and less sterically hindered so as to be able to react with the nucleophile. The rate of reaction depends on the concentration of the electrophile, which first has to undergo bond cleavage for before the nucleophile can approach. The rate of reaction is thus expressed as follows:

$$R = k[RX]$$

Recall that a carbocation has an empty p orbital with a lobe on either side of the carbon. The carbocation can be attacked equally on either lobe of the empty p orbital by the nucleophile. For non-chiral substrates the carbocation formed leads to the same product.

For chiral substrates, the resulting carbocation is still chiral and attack on the empty p orbital will lead to 50:50 mixture of mirror image products (enantiomers) with opposite configurations. Since enatiomers rotate the plane of polarized light in opposite directions the mixture of reaction products has zero optical activity. Such a mixture of equal amounts of mirror images is called a **racemic** mixture. The following reaction mechanism elucidates clearly the S_N2 reaction leading to formation of racemic mixture:



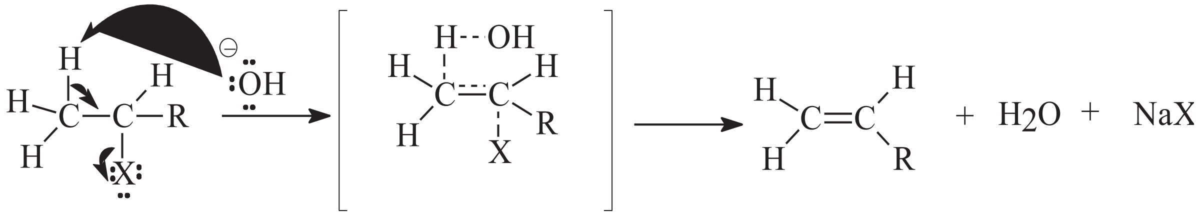
The electrophile (I) ionizes through C-Br bond cleavage to form a more stable tertiary carbocation (II), which is trivalent and less hindered. Attack by hydroxide ion occurs equally on either side of the empty p orbital to form an equal mixture of mirror images (III and IV) with opposite configuration. One enantiomer (III) retains the configuration of the starting material (I) with the nucleophile on the same place previously occupied by the leaving group (retention of configuration). The other enantiomer (IV) has an inverted configuration with the new group on the opposite side previously occupied by the leaving group (inversion of configuration). Apply your knowledge of assignment of configuration to stereogenic centres to assign R or S configuration to the substrate above.

8.4 Elimination reactions (E1 *versus* E2)

Elimination occurs between two adjacent carbon atoms, one bearing the leaving group and the other bearing a hydrogen atom to form an alkene. The leaving group departs from the opposite side (180˚) of the leaving proton (*trans*/*anti* elimination) to avoid electronic repulsions. Whenever two or more possible alkene products can be formed, the alkene with greater number of substituents around the two carbons of the double bond predominates (Zaitzev's rule).

8.4.1 E2 reaction of alkyl halides

Primary and secondary alkyl halides undergo second order elimination (E2) *via* a transition state with partial bond breakage firstly between carbon and the leaving groups and secondly between adjacent carbon and hydrogen, with simultaneous double bond formation between the two carbons. The leaving proton is abstracted by a base while at the same time the leaving group (halide ion) departs. Partial bond breakages (C–H and C–X) and bond formations (H–OH and C=C) occur simultaneously in the transition state. The leaving group departs from the opposite side (180˚) of the leaving proton (*trans* elimination) to form a C-C double bond. This *trans* elimination serves to avoid electron repulsions between the departing and incoming electrons. This is a second order reaction and the rate of reaction depends on the concentration of the base and the alkyl halide (R = k[RX][Base]). Whenever two or more possible alkene products to be formed, the alkene with the greater number of substituents around the two carbons of the double bond predominates (Zaitzev's rule).



X = F, Cl, Br or I

8.4.2 E1 Reaction of Alkyl Halides

This first order elimination (E1) reaction is restricted to tertiary alkyl halides and the reaction proceeds through a relatively stable tertiary carbocation. The C-X bond breaks to generate a more stable tertiary carbocation. The latter then undergoes loss of a proton from a carbon adjacent to the carbocation center to form an alkene. If a mixture of alkene products is to be formed, the most substituted alkene product dominates (Zaitzev's law).

Summary

You should now be able to formulate and describe physical and chemical properties of alkyl halides.

More specifically, you should be able to:

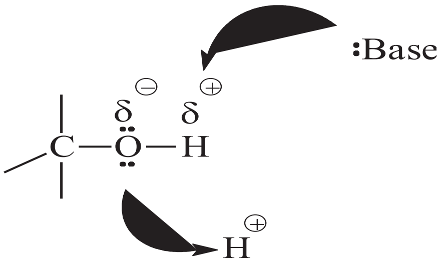
- Describe generalized structure of alkyl halides is described and apply the rules for naming them.
- Describe the preparation and classification of alkyl halides (primary, secondary and tertiary alkyl halides).
- Formulate and describe mechanisms for nucleophilic substitution of alkyl halides and to form alcohols and ethers.
- Formulate and describe mechanisms of elimination reactions of alkyl halides to form alkenes.

STUDY UNIT 9

Alcohols and Ethers

9.1 Generalized description of alcohols

Alcohols are characterized by the hydroxyl group (OH) bonded to a saturated, sp^3 hybridized carbon atom. The difference in electronegativity between oxygen and hydrogen makes oxygen slightly negative and hydrogen slightly positive. Oxygen is electron rich and therefore a site for attack by electron deficient species, e.g. protons (H^+). On the other hand, the electron poor hydrogen atom of the hydroxyl group can be easily deprotonated by a base to form an alkoxide ion ($^-$O-R). Thus alcohols have an amphoteric character and they can therefore serve as both acids and bases.



The common name of an alcohol consists of a name of the alkyl group to which the OH group is attached, followed by the word “alcohol”.

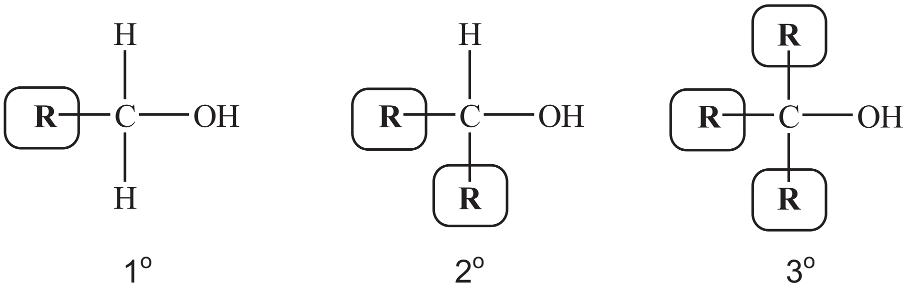
CH_3CH_2OH	$CH_3CH_2CH_2OH$
Ethyl alcohol	**Propyl alcohol**

The OH group is the functional group – the centre of reactivity of an alcohol. The IUPAC system uses the suffix “ol” to denote the OH group. Therefore, the systematic name of an alcohol is obtained by replacing the “e” at the end of the name of the parent hydrocarbon with the suffix “ol”. This should remind you of the use of the suffix “ene” to denote the functional group of an alkene.

CH_3CH_2OH	$CH_3CH_2CH_2OH$
Ethanol	**Propanol**

9.2 Classification of alcohols

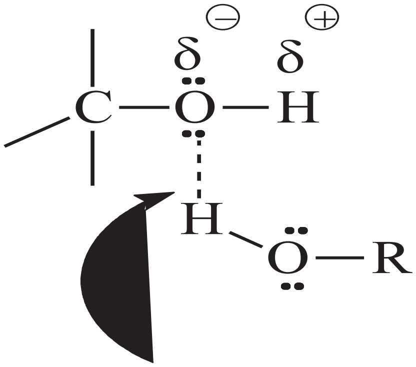
Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) alcohols, depending on the number of alkyl groups bonded to the hydroxyl-bearing carbon.



9.3 Physical properties of alcohols

Alcohols are quite different from the hydrocarbons and alkyl halides we have studied thus far. Not only is their chemistry much richer, but their physical properties are different as well. For example, 1-propanol, butane and chloroethane are close in molecular weight, yet 1-propanol boils at 97^{o}C, compared to -0,5^{o}C for the alkanes and 12,5^{o}C for the chloroalkane. WHY?

Alcohols have high boiling points because the **polar covalent bond** of alcohols can enable hydrogen to participate in **hydrogen bonding**. Hydrogen bonding can take place between a negatively polarized oxygen atom and a positively polarized hydrogen atom of another molecule.



Hydrogen bond

Hydrogen bonding involves weak van der Waals forces of attraction and energy in the form of heat is required to dissociate the hydrogen-bonded molecules, hence, such molecules have high boiling points. Another example is water with a molar mass of 18g/mol and boiling point of 100° C due to hydrogen bonding.

9.4 Preparation of alcohols

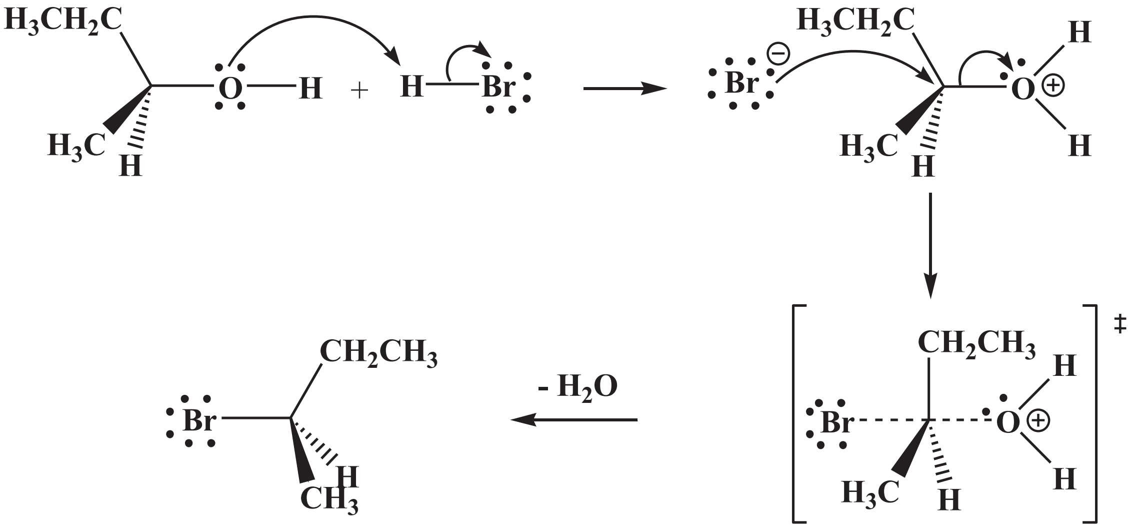
Alcohols can be prepared by acid catalyzed hydration of alkenes or nucleophilic substitution reactions of alkyl halide with hydroxide ions ($^{-}$OH) as described before.

9.5 Reactions of alcohols (nucleophilic substitution reactions)

Unlike in the case of alkyl halides, the electronegativities of carbon and oxygen in the C–O bond of alcohols differ slightly and therefore require oxygen to be protonated first before it can break away as water. Note that water in this case is a better leaving group than the hydroxide ion ($^{-}$OH) would have been.

9.5.1 S_N2 reaction of alcohols

Primary and most secondary alcohols (e.g. secondary butanol) in the mechanism below) are less sterically hindered for reverse-side attack and therefore undergo S_N2 reaction through a transition state. Protonation of alcohols by hydrogen halides, e.g. HBr occurs in the fist step to form a protonated alcohol. The positively charged oxygen is more electron withdrawing than that in the parent alcohol and thus makes the adjacent carbon more electrophilic for attack by a halide ion. In the second step, the protonated alcohol undergoes reverse-side attack by the bromide ion causing the cleavage of the C–O bond to release a good leaving group, water. This reverse-side attack occurs at 180˚ to the leaving group to avoid electron-electron repulsion in the transition state. In the transition state there is partial bond formation between C and Br and partial bond breakage between C and O. Water is released to form a secondary alkyl halide with inverted stereochemistry.



This is a second order reaction with the rate of reaction expressed as follows:

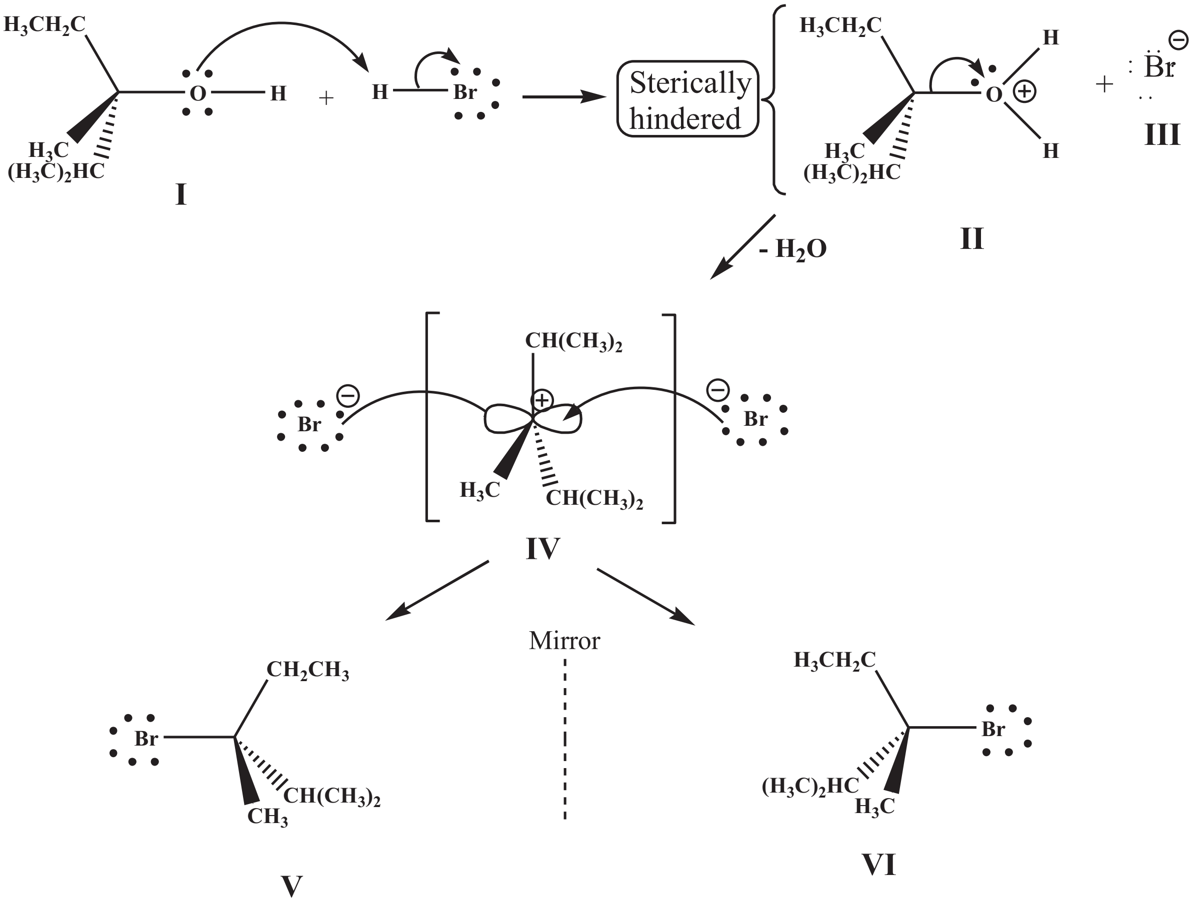
$$R = k[ROH_2]^+[Nu]$$

The progress of the reaction depends on the concentration of the protonated alcohol and the nucleophile.

9.5.2 S_N1 reaction of alcohols

Tertiary alcohols are more sterically hindered for reverse-side attack and they undergo S_N1 reactions with the formation of a more stable tertiary carbocation. Because of similar electronegativities of carbon and oxygen, the C–O bond needs to be protonated first before it can break to release water and to form a more stable tertiary carbocation. The reverse-side of a protonated tertiary alcohol is also too sterically hindered for attack by the nucleophile. Therefore bond cleavage occurs with the release of water to form a more stable tertiary carbocation with an empty p orbital which has a lobe on either side of the carbon atom. The following reaction mechanism elucidates clearly the S_N1 reaction of tertiary alcohols with HBR:

Step 1 involves protonation of oxygen atom of the alcohol (I) to form a protonated alcohol (II) with the release of the bromide ion (III). Bond breakage occurs between C and O to release water and a more stable tertiary carbocation (IV) with an empty p orbital. The bromide ion released in step 1 serves as a nucleophile and attacks the carbocation equally from either side to form an equal amount of mirror images (V and VI). These enantiomers have opposite configurations, with one of the enantiomer (VI) retaining the configuration of the substrate and the other (V) with inverted configuration. One enatiomer rotates the plane of polarized light to the positive side and the other to the negative side resulting in zero optical activity. Hence, it is called a racemic mixture. *Assign R and S configuration to the substrate and the two products*.

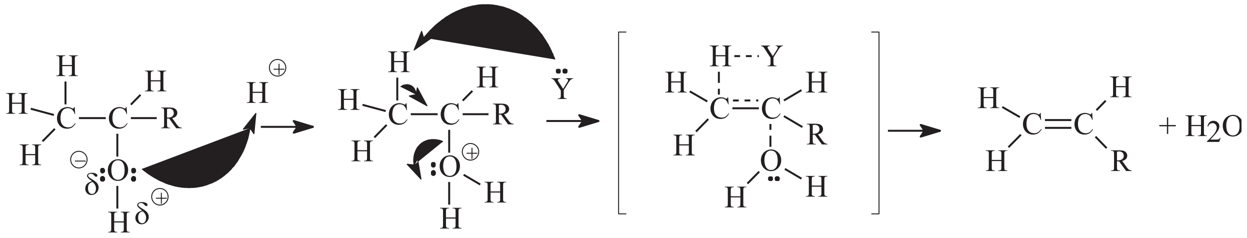


9.6 Elimination reactions of alcohols (E1 versus E2)

Elimination of water from alcohols occurs between two adjacent carbon atoms, one bearing the leaving group and the other bearing a hydrogen atom to form alkene moiety. Primary and secondary alcohols undergo E2 elimination via a transition state with partial bond breakage between carbon and the leaving group (water portion) and also between adjacent carbon and hydrogen atom with simultaneous double bond formation between the two carbons. On the other hand, tertiary alcohols undergo E1 reactions through a carbocation intermediate to form alkene product(s). In both cases, the leaving group departs from the opposite side (180˚) of the leaving proton (*trans* elimination) to avoid electron repulsions. Whenever two or more possible alkene products can be formed, the alkene with many substituents about the two carbons of the double bond predominates (Zaitzev's rule).

9.6.1 E2 reaction of alcohols

Primary and most secondary alcohols undergo E2 elimination via a transition state with partial bond breakage between carbon and the leaving groups (water) and also between adjacent carbon and hydrogen atom with simultaneous double bond formation between the two carbons. The leaving group departs from the opposite side (180˚) of the leaving proton (trans elimination) to avoid electron repulsions. Primary (R = H) and most secondary (R = alkyl) alcohols undergo protonation first to convert the hydroxyl group into a good leaving group, i.e. water. Then 1,2-elimination of water and one proton on the adjacent carbon occurs simultaneously from opposite sides of the carbon framework.



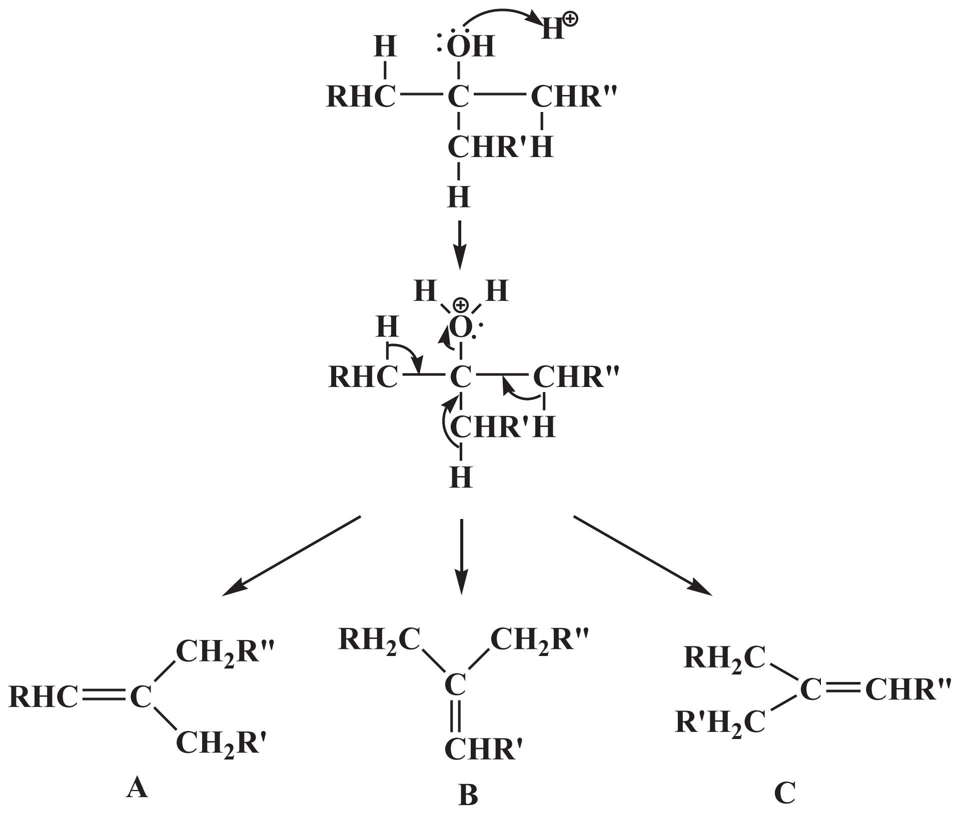
This is a second order reaction and the rate of reaction depends on the concentration of the protonated alcohol (ROH_2^+)and the base (Y):

$$R = k[ROH_2^+][Y]$$

Whenever two or more possible alkene products can be formed, the alkene with many substituents about the two carbons of the double bond predominates (Zaitzev's rule).

9.6.2 E1 reaction of alcohols

E1 reactions are restricted to tertiary alcohols and they proceed through a relatively stable tertiary carbocation. The carbocation undergoes loss of proton from a carbon adjacent the carbocation center to form an alkene.



If a mixture of alkene products is to be formed, the most substituted alkene product predominates (Zaitzev's rule).

This is a first order reaction and the rate of reaction depends on the concentration of the protonated alcohol only:

$$R = k[ROH_2^+].$$

9.7 Generalized description of ethers

Ethers are alcohol derivatives, which are characterized by the presence of an alkyl group (R) which is attached to the oxygen atom in place of the H which is found in alcohols. Ethers are non-polar and thus cannot participate in any hydrogen bonding. Consequently, ethers have lower boiling and melting points than alcohols of the same molar mass.

Their non-polar nature ethers less reactive and they are therefore suitable solvents for most chemical reactions.

9.7.2 Preparation of Ethers

Ethers can be prepared from alkenes through acid catalyzed reaction with alcohols. They can also be prepared from alkyl halides by nucleophilic substitution with alcohols or alkoxide ions. Other methods for the preparation of ethers from aldehydes and ketones will be discussed later.

Summary

You should now be able to formulate and describe physical and chemical properties of alcohols and ethers.

More specifically, you should be able to:

- Describe and compare generalized structures of alcohols and ethers and the rules for naming them.
- Desribe the preparation and classification of alcohols.
- Evaluate and compare the effect of hydrogen bonding on the physical properties of alcohols and ethers.
- Formulate and describe mechanisms for nucleophilic substitution of alcohols to form alkyl halides and ethers.
- Formulate and describe mechanisms of acid catalyzed elimination reactions (dehydration) of alcohols to form alkenes.
- Highlight generalised description of ethers and their preparations.

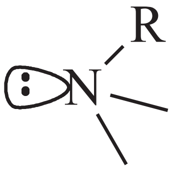
STUDY UNIT 10

AMINES

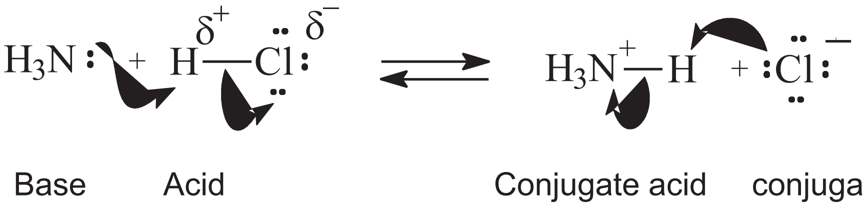
10.1 Generalized description of the structure of amines and their basicity

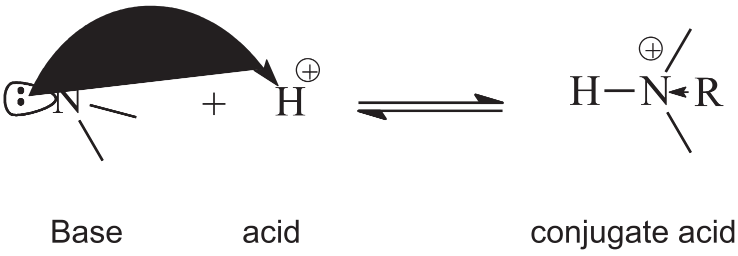
10.1 Generalized description of the structure of amines and their basicity

Amines are ammonia derivatives in which one or both hydrogen atoms on the N in ammonia have been replaced by a carbon-containing group.



As in ammonia, amines also contain a lone electron pair on N, which is responsible for their basicity. Electron donating groups attached to N push the electron density towards nitrogen; thereby making it more electron rich and thus more basic. On the other hand, electron withdrawing groups pull the electron density away from nitrogen thereby reducing its basicity. In methyl amine, for example, the methyl group pushes electron density towards N making the entire molecule more basic than ammonia. Steric hindrance around N in tertiary amines may reduce their capacity to deprotonate an acid and thereby resulting in reduced basicity compared to other amines. On the other hand, electron-donating groups also reduce the positive character of the resulting conjugate acid and thus stabilizing it. The more stable the conjugate acid, the more basic is the parent base from which it is derived.

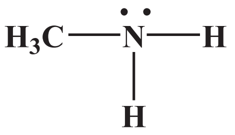




Amines are classified as primary (RNH_2), secondary (R_2NH), or tertiary (R_3N), depending on the number of alkyl substituents attached to nitrogen.

Primary amines are named using either systematic (IUPAC) or common names.

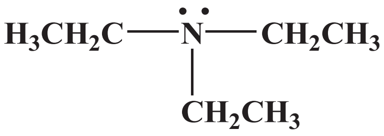
To assign the IUPAC name, find the longest continuous carbon chain bonded to the amine nitrogen, and change the **-e** ending of the parent alkane to the suffix ***–amine.*** Then use the usual IUPAC rules to number the chain and name the substituents. To assign a common name, name the alkyl group bonded to the nitrogen atom and add the word ***-amine***, forming a single word.



$$H_3C-\underset{\displaystyle H}{\underset{|}{\ddot{N}}}-H$$

IUPAC name: methanamine
Common name: methylamine

Secondary and tertiary amines with identical alkyl groups are named like the corresponding primary amine with prefix di- or tri- representing the number of identical alkyl groups attached to N. The example below has three ethyl groups attached to nitrogen and therefore the name is triethylamine.



$$H_3CH_2C-\underset{\displaystyle CH_2CH_3}{\underset{|}{\ddot{N}}}-CH_2CH_3$$

Triethylamine

Activity

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1. Use curved arrows to illustrate the movement of electrons during interconversion of the resonance structure of aminobenzene (aniline)
2. Use electronic factors to explain in detail why aniline is less basic than methylamine.

Summary

You should now be able to formulate and describe physical and chemical properties of amines.

More specifically, you should be able to:

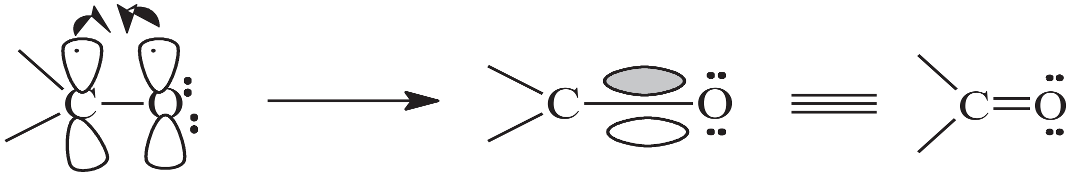
- Describe the generalized structure of amines is described and apply the rules for naming them.
- Describe and compare the basicity of amines and their conjugate states.

STUDY UNIT 11

Carbonyl compounds and their derivatives

11.1 Generalized description of ketones and aldehydes
11.1 Generalized description of ketones and Aldehydes
11.2 Reactivity of the carbonyl group
11.3 Generalized description of carboxylic acids
11.4 Nomenclature of carboxylic acids
11.5 Acidity of carboxylic acids
11.6 Generalized description of esters, amides, acid halides and anhydrides

Ketones and aldehydes are characterized by a C-O double bond (carbonyl group). Both carbon and oxygen of the double bond are sp^2 hybridized with carbon bonded to oxygen and two other atoms by single bonds by means of the three sp^2 orbitals. The three single bonds formed through head-on overlap of sp^2 orbitals are the sigma bonds. Each of the remaining p orbitals on carbon and oxygen contains a single electron and has a lobe above and below the sigma framework. The two orbitals which lie parallel to each other overlap sideways to form a weak pi bond.



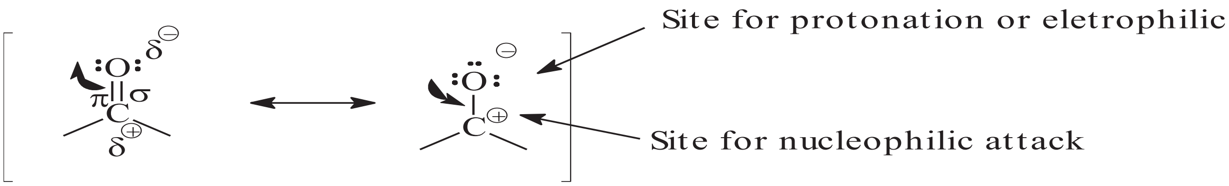
sideways overlap

pi electron cloud above and below the sigma framework

The bond angles around the carbonyl group are 120° and the geometry is trigonal and planar (flat). The electrons of the pi bond are weakly held and are concentrated largely around oxygen atom. The C-O double bond is polarized with a partial positive charge on C and a partial negative charge on O (Why?).

11.2 Reactivity of the carbonyl group

Carbon is electrophilic and is a site for attack by nucleophiles. On the other hand, oxygen is more negative and it can be attacked by electrophiles or acids.



In any acid catalyzed carbonyl addition to an aldehyde or ketone, the catalyst which is usually H^+ kick-starts the reaction and is attacked by the negatively charged carbonyl oxygen to form a resonance stabilized carbonyl compound. The latter is more electronegative than the parent aldehyde or ketone. Then the protonated carbonyl compound is trivalent and trigonal and can be attacked by the nucleophile to form a tetravalent species which is tetrahedral.

Remember that reactivity at the target carbon is influenced by the size of the surrounding atoms (steric hindrance) and electronic factors (inductive and/ or resonance effect) of the surrounding substituents. Electron donating groups reduce electrophilicity of carbon whereas electron withdrawing groups make carbon more electron poor and therefore more electrophilic for attack by nucleophiles. Follow this argument and then try to provide a detailed explanation why aldehydes are more reactive than ketones.

Activity:

(a) Draw the resonance structures of propanone in the ground state indicating bond polarity with partial or full charges.

(b) React propanone with a mineral acid catalyst (H^+) and draw the resonance structures of the protonated propanone.

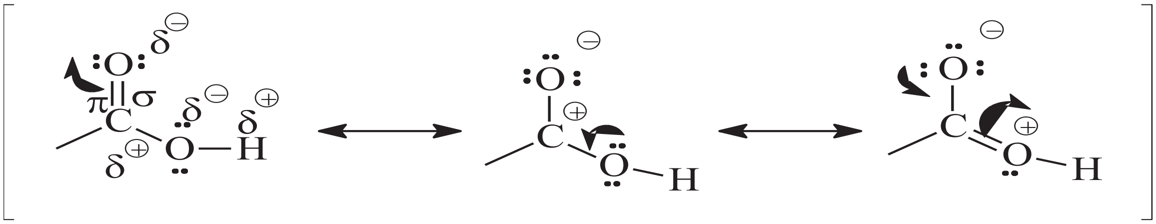
(c) What are the net charges of the ground state and the protonate structures drawn above?

(d) Which of the resonance states (ground or protonated) is more electrophilic (i.e. more reactive)?

Students must be able to distinguish between an aldehyde and a ketone and how to name them (IUPAC rules).

11.3 Generalized description of carboxylic acids

Carboxylic acids are characterized by a hydroxyl group (OH) attached to the carbon of the polar carbonyl group. When the carbonyl oxygen pulls the pi electrons towards itself, it renders the carbonyl carbon electron deficient and positive. Oxygen of the hydroxyl group donates the pair of electrons to carbon to form a double bond. This interaction renders the hydroxyl oxygen positive. It however fulfills octet state or noble gas configuration even though it bears a positive charge. Note that the positive charge is equally (50:50) distributed on the carbonyl carbon and oxygen or nitrogen.



Carbon positively charged

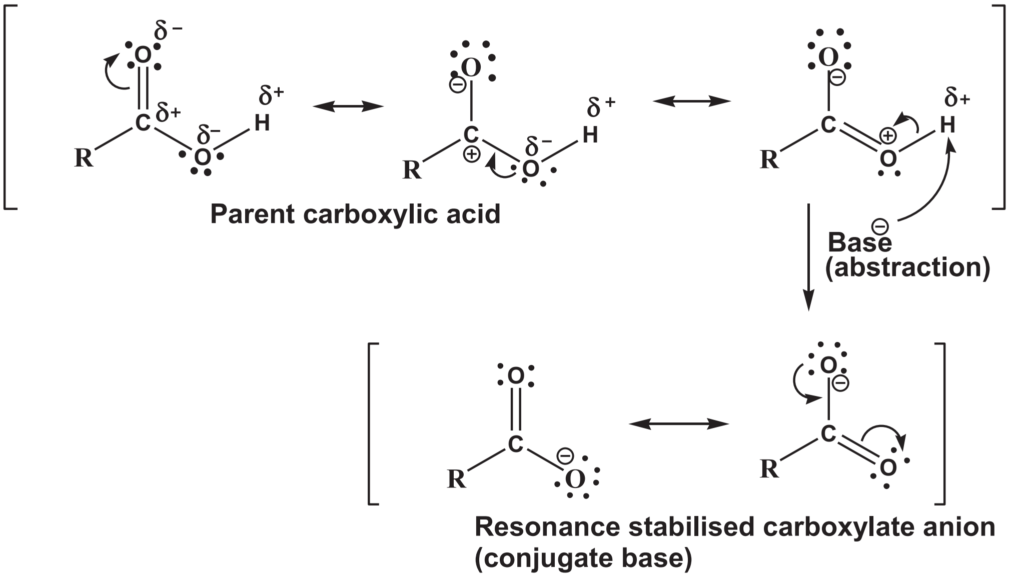
Oxygen positively charged

11.4 Nomenclature of carboxylic acids

The carboxylic group takes priority over the other functional groups and it is always considered the parent functional group.

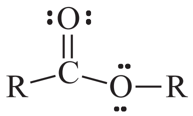
11.5 Acidity of carboxylic acids

The positively charged oxygen is strongly electron withdrawing and it makes the hydroxyl hydrogen more electron poor. An electron poor hydroxyl hydrogen is strongly acidic for abstraction by a base to form a carboxylate ion (RCO_2^-). The carboxylate ion is resonance stabilized with the negative charge distributed equally on the two oxygen atoms. The more resonance structures are possible the more stable the species is. The carboxylate ion (RCO_2^-) is a conjugate base and is stabilized by resonance effect. The more stable the conjugate base the more acidic is the parent acid is from which it is derived. Thus carboxylic acids are more acidic than alcohols.

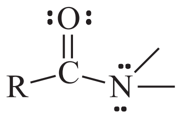


11.6 Generalized description of esters, amides, acid halides and anhydrides

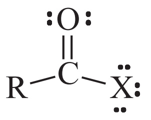
Carboxylic acid derivatives are characterized by a polar carbonyl group attached to an alkoxy group (OR) for esters, amino group (NH_2, NHR, NR_2) for amides, a halogen (X = Cl, Br) for acid halides or carboxyl group for acid anhydrides.



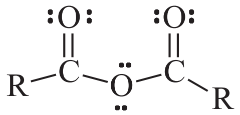
Esters



amides



acid halides



acid anhydrides

Except for acid halides, the other acid derivatives are less reactive than aldehydes and ketones.

Draw all the resonance structures of the above acid derivatives and compare the number of possible resonance hybrids with those of aldehydes and ketones. Note that the more resonance structures are possible, the greater the stability is of these carbonyl derivatives.

Summary

You should now be able to describe the electronic structure and physical properties of ketones and aldehydes, carboxylic acids, esters, acid halides, amides and anhydrides and their physical properties.

More specifically, you should be able to:

- Construct generalized structures of aldehydes and ketones and compare their bond polarity.
- Apply rules for naming aldehydes and ketones.
- Construct generalized structures of carboxylic acids, esters and amides and apply the rules for naming carboxylic acids, esters and amides.
- Describe acidity of carboxylic acids and their conjugate bases.

END OF STUDY GUIDE