SRINIVASAN COLLEGE OF ARTS AND SCIENCE

PERAMBALUR-621212

(Affiliated to Bharathidasn University-Tiruchirappalli)

DEPARTMENT OF CHEMISTRY

COURSE MATERIAL

PROGRAGMME : UG

SUBJECT : GENERAL CHEMISTRY IV

SUBJECT CODE : 16SCCCH4

SEMESTER : EVEN SEM

SYLLABUS

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GENERAL CHEMISTRY IV

OBJECTIVES

1. To learn the general characteristics of d and f block elements.
2. To understand the reactions of organometallic compounds, alcohols, phenols and ethers.
3. To learn about the fundamental concepts of first law of thermodynamics, to relate heat, work and energy and to calculate work from pressure – volume relationships.
4. To learn about the fundamental concepts of rate of the reaction, determination of order of the reaction and theories of reaction rates.

UNIT I d-BLOCK & f-BLOCK ELEMENTS

1.1 General characteristics of d-block elements, comparative study of zinc group elements, extraction of Mo & Pt - Alloys of copper, amalgams and galvanization. Evidences for the existence of 2+ Hg 2 ions.

1.2 General characteristics of f-block elements – Lanthanide contraction and its consequences. Extraction of Th.

1.3 Arrhenius, Lowry – Bronsted and Lewis concept of acids and bases.

UNIT II CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

2.1 Introduction – preparation of organomagnesium compounds- physical and chemical properties- uses. Organozinc compounds – general preparation, properties and uses.

2.2 Organolithium, organocopper compounds – preparation, properties and uses.

2.3 Organolead, organophosphorous and organoboron compounds– preparation, properties and uses.

UNIT III CHEMISTRY OF ALCOHOLS, PHENOLS AND ETHERS

3.1 Nomenclature – industrial source of alcohols – preparation of alcohols: hydration of alkenes, oxymercuration, hydroboration, Grignard addition, reduction – physical properties – chemical properties - uses – glycols from dihydroxylation, reduction, substitution reactions and glycerols and their uses.

3.2 Preparation of phenols including di- and trihydroxy phenols – physical and chemical properties - uses – aromatic electrophilic substitution mechanism – theory of orientation and reactivity.

3.3 Preparation of ethers: dehydration of alcohols, Williamson's synthesis – silyl ether. epoxides from peracids - sharpless asymmetric epoxidation – reactions of epoxides – uses – introduction to crown ethers – structures – applications.

UNIT IV THERMODYNAMICS-I

4.1. Definitions- system and surrounding- isolated, closed and open system- state of the system- Intensive and extensive variables. Thermodynamic processes-reversible and irreversible, isothermal and adiabatic processes- state and path functions.

4.2. Work of expansion at constant pressure and at constant volume. First law of thermodynamics- statement- definition of internal energy (E), enthalpy (H) and heat capacity. Relationship between Cp and Cv.

4.3. Calculation of w, q, dE and dH for expansion of ideal and real gases under isothermal and adiabatic conditions of reversible and irreversible processes.

4.4. Thermochemistry- relationship between enthalpy of reaction at constant volume (qv) and at constant pressure (qp)- temperature dependence of heat of reactionKirchoff's equation-bond energy and its calculation from thermochemical dataintegral and differential heats of solution and dilution.

UNIT V CHEMICAL KINETICS

5.1. Rate of reaction- rate equation, order and molecularity of reaction. Rate Lawsrate constants-derivation of first order rate constant and characteristics of zero order, first order and second order reactions- derivation of time for half change (t1/2) with examples.

5.2. Methods of determination of order of reactions- experimental methodsdetermination of rate constant of a reaction by volumetry, colorimetry and polarimetry.

5.3. Effect of temperature on reaction rate- concept of activation energy, energy barrier, Arrhenius equation. Theories of reaction rates- collision theory- derivation of rate constant of bimolecular reaction- failure of collision theory- Lindemann's theory of unimolecular reaction.

5.4. Theory of absolute reaction rates – derivation of rate constant for a bimolecular reaction- significance of entropy and free energy of activation. Comparison of collision theory and absolute reaction rate theory (ARRT).

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UNIT I

d-BLOCK & f-BLOCK ELEMENTS

D block elements are the elements which can be found from the third group to the twelfth group of the modern periodic table. The valence electrons of these elements fall under the d orbital. D block elements are also referred to as transition elements or transition metals.

Elements having electrons (1 to 10) present in the d-orbital of the penultimate energy level and in the outer most ‘s’ orbital (1-2) are **d block elements.** Although electrons do not fill up ‘d’ orbital in the group 12 metals, their chemistry is similar in many ways to that of the preceding groups, and so considered as d block elements.

These elements typically display metallic qualities such as malleability and ductility, high values of electrical conductivity and thermal conductivity, and good tensile strength. There are four series in the d block corresponding to the filling up of 3d, 4d, 5d or 6d orbitals.

- 3d- Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
- 4d- Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd
- 5d- La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg
- 6d- incomplete.

There are 10 elements filling up the ‘d’ orbital in each series.

General characteristics of d-block elements:

All the elements of the D-block show similar properties due to the presence of similar electronic configuration of the outermost shell. The outermost shell configuration is ns^2. Here is a list of general properties such as the atomic and ionic radii, electronic configuration and the ionisation potentials observed among the D-block elements.

1. **Metallic nature**: as the number of electrons in the outermost shell is very less i.e. All the transition elements are metals. They show the characteristics of metals such as malleability and ductile in nature and form alloys with several other metals. They also serve as good conductors of heat and electricity. Except for Mercury which is liquid and soft like alkali metals all the transition elements are hard and brittle unlike the non-transition elements. The

hard and brittle nature of these elements indicates the presence of covalent bond which is due to the presence of unfilled d-orbitals. However, their property such as good conductivity is an indication for the presence of metallic bonding. Hence, they are said to form covalent bonding as well as the metallic boding.

2. **Melting and boiling points**: They show very high melting and boiling points. This can be attributed to the presence of strong metallic bonding due to the overlapping of (n-1) d orbitals and covalent bonding of the unpaired d orbital electrons. Since Zn, Cd and Hg have completely filled (n-1)d orbitals they are not expected to form covalent bonds. Hence, they show comparatively lower melting point than other d-block elements.

3. **Atomic radii**: a great degree of variation is seen in the atomic radii across each transition series. The atomic radii of the d-block elements within a given series decreases with increase in the atomic number. This is due to the increase in the nuclear charge that attracts the electron cloud inwards resulting in decrease in size. However, the decrease a uniform decrease in atomic radius is not observed across a period. The decrease in atomic radii is small compared to the S and P block elements. This is due to the screening effect caused by the electrons of the (n-1)d subshell on the outermost shell. As a result the nucleus cannot pull the outermost electrons. Thus, the size of the atom does not alter much in moving from Cr to Cu.

   The atomic radius increases on descending the group. In a given series, the atomic radius decreases to a minimum for the group VIII elements and then it increases towards the end of the series. This increase in radius towards the end of the series is due to the force of repulsion among the added electrons. A close similarity is observed in the radii of the elements of the second and third transition series due to the filling of 4f subshells.

4. **Ionic radi**i: The ionic radius is similar to the pattern of atomic radii. Thus, for ions of a given charge the radius decreases slowly with increase in atomic number.

5. **Atomic volume and Densities**: the atomic volume of transition elements is much lower than those of S and P block elements. This is because of the filling of the (n-1)d orbitals that cause an increase in the nuclear charge and pulls the electrons inward. This results in decrease in atomic volume. With the decrease in the atomic volume, the atomic density of these elements increases. Osmium is having a maximum density.

   In a given transition series, the density increases in moving across the period and reaches a maximum value at group VIII.

   The density increases as we move down the group. The atomic sizes of elements of the second and third transition series are nearly same but their atomic weights increase nearly two fold and the densities of elements of third transition series are generally twice of the corresponding second transition series.

6. **Ionization potentials**: Transition elements have high ionization energy due to their small size. Their ionization potentials lie between those of S and P block elements. Thus, they are less electropositive than the s-block elements. Hence, they do not form ionic compounds readily like the alkali and alkaline earth metals. They also have the ability o form covalent compounds.

   The ionisation potentials of d-block elements increase as we move across each series from left to right. However, the increase is not as much as in case of S and P blocks elements. This is due to the screening effect caused by the new electrons that are added into the (n-1) d subshell.

   The second ionisation energies of the first transition series also increases with the increase in atomic number. However, Cr and Cu are sufficiently higher than those of their neighbours. This is due to their stable electronic configuration.

7. **Electronic configuration**: the outer electronic configuration remains constant. But, a electron is added to the penultimate shell till the d-sub shell reaches its full capacity. There are three series of elements depending on the n-1 d orbital that is being filled. The orbitals are filled in order of their increasing energy i.e. an orbital of lower energy is filled first. Thus 4s orbital with lesser energy is filled first to its full extent then the 3d orbital with higher energy is filled. The exactly half-filled and completely filled d-orbitals are extra stable.

   The electronic configuration of the first series is given as $1s^2 2s^2 p^6\ 3s^2 p^6 d^{1\text{-}10}\ 4s^2$

   The electronic configuration of the second series is given as $1s^2 2s^2 p^6\ 3s^2 p^6 d^{1\text{-}10}\ 4s^2 p^6 d^{1\text{-}10}\ 5s^2$

   The electronic configuration of the third series is given as $1s^2 2s^2 p^6\ 3s^2 p^6 d^{1\text{-}10}\ 4s^2 p^6 d^{1\text{-}10}\ 5s^2 p^6 d^{1\text{-}10}\ 6s^2$

   Transition elements also show variable oxidation states, tendency to form complexes, magnetic nature and other properties.

Comparative Study of Zinc Group Elements:

Zinc group element, any of the four chemical elements that constitute Group 12 (IIb) of the periodic table—namely, zinc (Zn), cadmium (Cd), mercury (Hg), and copernicium (Cn). They have properties in common, but they also differ in significant respects. Zinc, cadmium, and mercury are metals with a silvery-white appearance and relatively low melting points and boiling points.

Mercury is the only common metal that is liquid at room temperature, and its boiling point is lower than that of any other metal.

Zinc, cadmium, and mercury can lose the two electrons in the outermost shell to form dipositive ions, M^{2+} (in which M represents a generalized metal element), thereby exposing the next innermost shell with a stable configuration in each case of 18 electrons.

These three elements tend to use the two outer electrons for covalent bonding.

Zinc exhibits only the +2 oxidation state. It can give up two electrons to form an electrovalent compound; e.g., zinc carbonate $ZnCO_3$. It may also share those electrons, as in zinc chloride, $ZnCl_2$, a compound in which the bonds are partly ionic and partly covalent.

Cadmium compounds are mainly ionic, but cadmium also forms complex ions with ligands (atoms, ions, or molecules that donate electrons to a central metal ion); e.g., the complex ion with ammonia NH_3, having the formula $[Cd(NH_3)_4]^{2+}$, or with the cyanide ion, the formula $[Cd(CN)_4]^{2-}$.

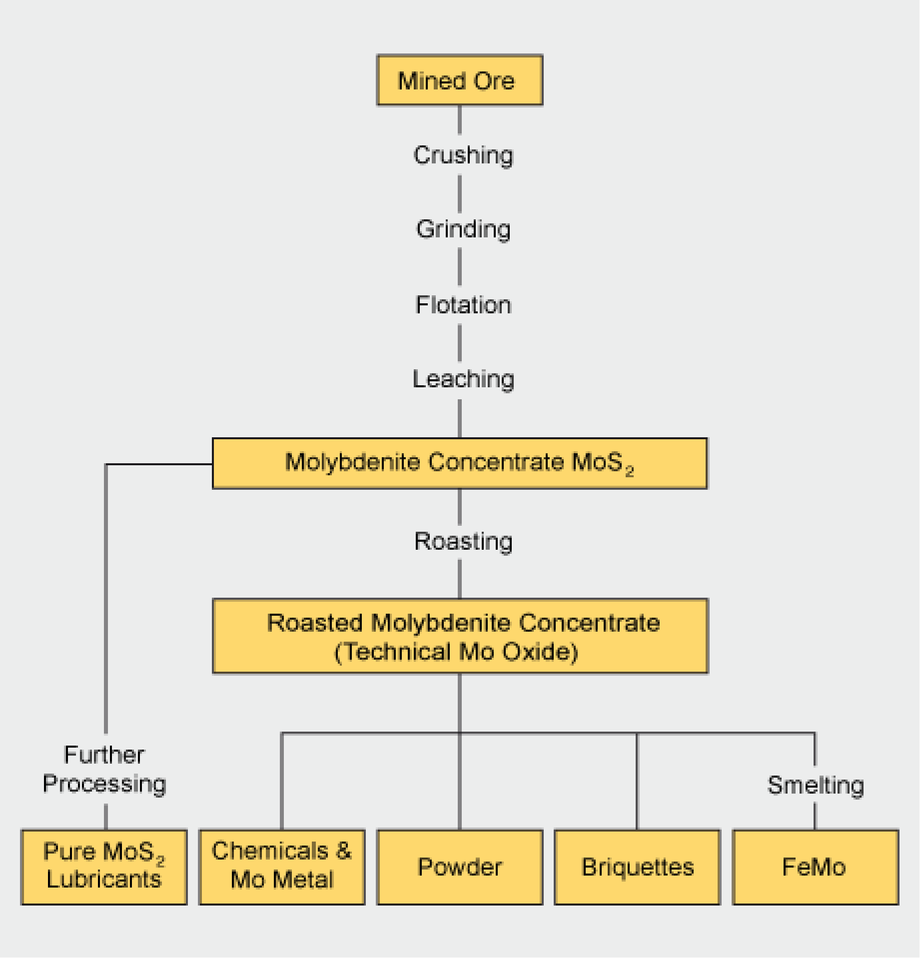
Mercury in its +2 and +1 oxidation states forms the ions Hg^{2+} and $[Hg_2]^{2+}$, respectively. In the latter, two electrons are shared in a covalent bond between the two metal atoms. The $[Hg_2]^{2+}$ ion shows little tendency to form complexes, whereas the Hg^{2+} ion does form them. In contrast to compounds of mercury in the +2 state, which are usually covalent, all the common salts of mercury in the +1 state are ionic, and the soluble compounds—e.g., mercurous nitrate, $Hg_2(NO_3)_2$—show normal properties of ionic compounds, such as ease of dissociation or breakup into separate ions in solution.

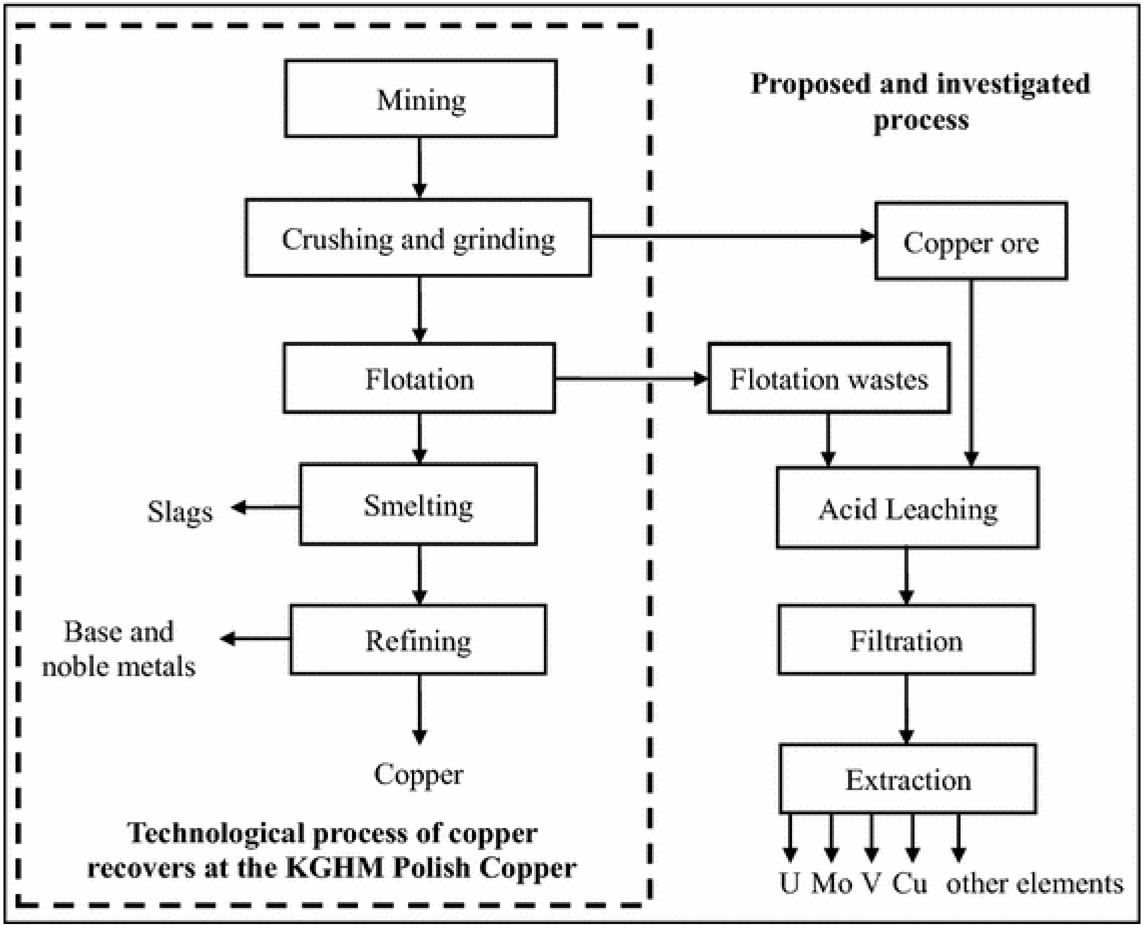
Mercury is exceptional in that, unlike zinc or cadmium, it does not react easily with oxygen on heating, and mercuric oxide does not show the acid property of forming salts (mercurates), whereas zinc oxide does this readily.

Extraction of Mo:

- Molybdenum can be found in a number of minerals, but only molybdenite is suitable for the industrial production of marketable molybdenum products. Molybdenite can occur as the sole mineralization in an ore body, but is usually associated with the sulphide minerals of other metals, mainly copper. Molybdenum mines are classified into three groups according to the minerals contained in the ore body and their quality:
- •Primary mines, where the extraction of molybdenite is the sole aim.
- •By-product mines, where the extraction of copper-bearing ores is the primary aim, and molybdenite extraction provides additional economic value.
- •Co-product mines, where both molybdenite and copper-bearing minerals are extracted.
- Roughly 40 percent of molybdenum comes from primary mines, with the other 60 percent a by-product of copper or, in some cases, tungsten.

- If the ore lies close to the surface, open-pit technology will be used, and if the ore lies deep underground, the underground method will be used.





Extraction of Pt:

Alloys of copper:

Copper alloys are metal alloys that have copper as their principal component. They have high resistance against corrosion. The best known traditional types are bronze, where tin is a significant addition, and brass, using zinc instead. Both of these are imprecise terms, having both been commonly referred to as lattens in the past. Today the term *copper alloy* tends to be substituted, especially by museums.

Classification of copper and its alloys

Family	Principal alloying element	UNS numbers
Copper alloys, brass	Zinc (Zn)	C1xxxx–C4xxxx,C66400–C69800
Phosphor bronze	Tin (Sn)	C5xxxx
Aluminium bronzes	Aluminium (Al)	C60600–C64200
Silicon bronzes	Silicon (Si)	C64700–C66100
Cupronickel, nickel silvers	Nickel (Ni)	C7xxxx

Amalgams:

An **amalgam** is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid, depending upon the proportion of mercury.

These alloys are formed through metallic bonding,with the electrostatic attractive force of the conduction electrons working to bind all the positively charged metal ions together into a crystal lattice structure.

Almost all metals can form amalgams with mercury, the notable exceptions being iron, platinum, tungsten, and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore. Dentistry has used alloys of mercury with metals such as silver, copper, indium, tin and zinc.

Important amalgams:

Zinc amalgam

Zinc amalgam finds use in organic synthesis (e.g., for the Clemmensen reduction).[3] It is the reducing agent in the Jones reductor, used in analytical chemistry. Formerly the zinc plates of dry batteries were amalgamated with a small amount of mercury to prevent deterioration in storage. It is a binary solution (liquid-solid) of mercury and zinc.

Potassium amalgam:

For the alkali metals, amalgamation is exothermic, and distinct chemical forms can be identified, such as KHg and KHg_2.KHg is a gold-coloured compound with a melting point of 178 °C, and KHg_2 a silver-coloured compound with a melting point of 278 °C. These amalgams are very sensitive to air and water, but can be worked with under dry nitrogen.

Sodium amalgam:

Sodium amalgam is produced as a byproduct of the chloralkali process and used as an important reducing agent in organic and inorganic chemistry.

With water, it decomposes into concentrated sodium hydroxide solution, hydrogen and mercury, which can then return to the chloralkali process anew. If absolutely water-free alcohol is used instead of water, an alkoxide of sodium is produced instead of the alkali solution.

Aluminium amalgam:

Aluminium can form an amalgam through a reaction with mercury. Aluminium amalgam may be prepared by either grinding aluminium pellets or wire in mercury, or by allowing aluminium wire or foil to react with a solution of mercuric chloride.

This amalgam is used as a reagent to reduce compounds, such as the reduction of imines to amines.

Tin amalgam:

Tin amalgam was used in the middle of the 19th century as a reflective mirror coating.

Other amalgams:

- Thallium amalgam has a freezing point of −58 °C, which is lower than that of pure mercury (−38.8 °C) so it has found a use in low temperature thermometers.
- Gold amalgam: Refined gold, when finely ground and brought into contact with mercury where the surfaces of both metals are clean, amalgamates readily and quickly to form alloys ranging from $AuHg_2$ to Au_8Hg.

Lead forms an amalgam when filings are mixed with mercury and is also listed as a naturally occurring alloy called leadamalgam in the Nickel–Strunz classification.

Dental amalgam:

Dentistry has used alloys of mercury with metals such as silver, copper, indium, tin and zinc. Amalgam is an "excellent and versatile restorative material" and is used in dentistry for a number of reasons. It is inexpensive and relatively easy to use and manipulate during placement; it remains soft for a short time so it can be packed to fill any irregular volume, and then forms a hard compound.

Galvanization:

Galvanization or **galvanizing** (also spelled **galvanisation** or **galvanising**) is the process of applying a protective zinc coating to steel or iron, to prevent rusting. The most common method is hot-dip galvanizing, in which the parts are submerged in a bath of molten hot zinc.

Protective action:

Galvanizing protects the underlying iron or steel in the following main ways:

- The zinc coating, when intact, prevents corrosive substances from reaching the underlying steel or iron.
- The zinc protects iron by corroding first. For better results, application of chromates over zinc is also seen as an industrial trend.
- In the event the underlying metal becomes exposed, protection can continue as long as there is zinc close enough to be electrically coupled. After all of the zinc in the immediate area is consumed, localized corrosion of the base metal can occur.

General characteristics of f-block elements:

F block elements are divided into two series, namely lanthanoids and actinoids. These block of elements are often referred to as **inner transition metals** because they provide a transition in the 6th and 7th row of the periodic table which separates the s block and the d block elements.

Elements whose f orbital getting filled up by electrons are called **f block elements**. These elements have electrons, (1 to 14) in the f orbital, (0 to 1) in the d orbital of the series.

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Properties of Lanthanide:

- Lanthanide Series
- Lanthanide Contraction
- Electronic Configuration
- Oxidation State of Lanthanides
- Chemical Reactivity
- Ionization Energy
- Physical Properties
- Formation of Coloured Ions
- Uses of Lanthanides

Lanthanides are highly dense metals with even higher melting points than d-block elements. They form alloys with other metals. These are the f block elements that are also referred to as the inner transition metals. The inner transition elements/ions may have electrons in s, d and f- orbitals.

In the periodic table like transition metal if we consider lanthanides and actinides series the table will be too wide. These two series are present in the bottom of the periodic table and they are called

4f series (Lanthanods series) and 5f series (Actanoids series). The 4f and 5f series together called inner transition elements.

All of the elements in the series closely resemble lanthanum and each another in their chemical and physical properties. Some of the key characteristics and properties are:

- They have a lustre and are silvery in appearance.
- They are soft metals and can even be cut with a knife
- The elements have different reaction tendencies depending on basicity. Some are very reactive while some take time to react.
- Lanthanides can corrode or become brittle if they are contaminated with other metals or non-metals.
- They all mostly form a trivalent compound. Sometimes they can also form divalent or tetravalent compounds.
- They are magnetic.

Lanthanide Contraction:

The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called **lanthanide contraction.**

Consequences of Lanthanide Contraction:

Following points will clearly depict the effect of lanthanide contraction:

- Atomic size
- Difficulty in the separation of lanthanides
- Effect on the basic strength of hydroxides
- Complex formation
- The ionization energy of d-block elements

1. Atomic size: Size of the atom of third transition series is nearly the same as that of the atom of the second transition series. For example: radius of Zr = radius of Hf & radius of Nb = radius of Ta etc.

2. Difficulty in the separation of lanthanides: As there is an only small change in the ionic radii of Lanthanides, their chemical properties are similar. This makes the separation of elements in the pure state difficult.

3. Effect on the basic strength of hydroxides: As the size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases. Thus, La (OH)3 is more basic and Lu(OH)3 is the least basic.

4. Complex formation: Because of the smaller size but higher nuclear charge, tendency to form coordinate. Complexes increases from La3+ to Lu3+.

5. Electronegativity: It increases from La to Lu.

6. Ionization energy: Attraction of electrons by the nuclear charge is much higher and hence Ionization energy of 5d elements are much larger than 4d and 3d. In 5d series, all elements except Pt and Au have filled s-shell.

Elements from Hafnium to rhenium have same Ionization Energy and after Ionization Energy increases with the number of shared d-electrons such that Iridium and Gold have the maximum Ionization Energy.

Case Study:

Mercury – the liquid metal: Mercury is the only metal that exists in its liquid state at room temperature. 6s valence electrons of Mercury are more closely pulled by the nucleus (lanthanide contraction) such that outer s-electrons are less involved in metallic bonding.

7. Formation of Complex: Lanthanides exhibiting 3+ oxidation state is the larger and hence low charge to radius ratio. This reduces the complex-forming ability of lanthanides compared to d-block elements. Still they, form complexes with strong chelating agents like EDTA, β-diketones, oxime etc. They do not form Pπ-complexes.

Electronic Configuration of Lanthanides:

Lanthanides of first f-block have a terminal electronic configuration of [Xe] 4f1-14 5d 0-16s2 of the fourteen lanthanides, promethium (Pm) with atomic number 61 is the only synthetic radioactive element. The energy of 4f and 5d electrons are almost close to each other and so 5d orbital remains vacant and the electrons enter into the 4f orbital.

Exceptions are in the case of gadolinium, Gd (Z = 64) where the electron enters the 5d orbital due to the presence of half-filled d-orbital and lutetium (Z = 71) enters the 5d orbital.

Oxidation State of Lanthanides:

All the elements in the lanthanide series show an oxidation state of +3. Earlier it was believed that some of the metals (samarium, europium, and ytterbium) also show +2 oxidation states. Further studies on these metals and their compounds have revealed that all the metals in lanthanide series exhibit +2 oxidation state in their complexes in solutions.

A few metals in the lanthanide series occasionally show +4 oxidation states. This uneven distribution of oxidation state among the metals is attributed to the high stability of empty, half-filled or fully filled f-subshells.

The stability of f-subshell affects the oxidation state of lanthanides in such a way that the +4 oxidation state of cerium is favoured as it acquires a noble gas configuration but it reverts to a +3 oxidation state and thus acts as a strong oxidant and can even oxidize water, although the reaction will be slow.

The +4 oxidation state is also exhibited by the oxides of:

- Praseodymium (Pr)
- Neodymium (Nd)
- Terbium (Tb)

- Dysprosium (Dy)

Europium (atomic number 63) has the electronic configuration [Xe] $4f^7$ $6s^2$, it loses two electrons from 6s energy level and attains the highly stable, half-filled $4f^7$ configuration and hence it readily forms Eu^{2+}ion. Eu^{2+} then changes to the common oxidation states of lanthanides (+3) and forms Eu^{3+}, acting as a strong reducing agent.

Ytterbium (atomic number 70) also has similar reasons for being a strong reducing agent, in the Yb^{2+} state; it has a fully filled f-orbital.

The presence of f-subshell has a great influence on the oxidation state exhibited by these metals and their properties. New developments and findings continue to add information on lanthanides.

The energy gap between 4f and 5d orbitals is large and so the number of oxidation states limited, unlike the d-block elements.

Energy level and in the outermost's orbital:

There are two series in the f block corresponding to the filling up of 4f and 5f orbitals. The elements are 4f series of Ce to Lu and 5f series of Th to Lw. There are 14 elements filling up the 'f' orbital in each series.

- Lanthanides
- Actinides

Classification of F Block Elements:

The elements belonging to the f block are further differentiated into:

1. The first series of elements are called **lanthanides** and include elements with atomic numbers beginning from 57 and ending at 71. These elements are non-radioactive (except for promethium, which is radioactive).

2. The second series of elements are called **actinides** and include elements with atomic numbers beginning from 89 and ending at 103. These elements generally have a radioactive nature.

The list of all the f block elements is provided below. The row beginning with Lanthanum is the row containing all the lanthanides whereas the row beginning with Actinium is the row that contains all the actinides.

F block Elements as Inner Transition Elements:

Since the f orbital lies much inside than d orbital, in relation to the transition metals naming, f block elements are called inner transition elements.

- Have electrons added to the ‘f’ sub-orbitals of (n-2) level
- Are placed between (n-1)d and ns block elements in the periodic table.
- Properties are similar to d-block elements.

- Lanthanides are soft metals with a silvery white colour.
- Their colour dulls and their brightness reduces rapidly when exposed to air.
- They have melting points ranging from 1000K to 1200K (Except Samarium, 1623K).
- Lanthanides are good conductors of heat and electricity.
- They are non-radioactive in nature with the exception of Promethium
- A decrease in atomic and ionic radii from lanthanum to lutetium is observed. This is called the lanthanoid contraction.

Properties of Actinides:

- The Actinide elements appear to be silvery in colour.
- These elements have a radioactive nature.
- These metals are highly reactive and their reactivity increases when they are finely divided.

- A decrease in atomic and ionic radii from Actinium to Lawrencium is observed. This is called the actinoid contraction.
- They generally exhibit an oxidation state of +3. However, elements belonging to the first half of the series are known to exhibit higher oxidation states quite frequently.

Difference between Lanthanides and Actinides:

- Lanthanoids are involved in the filling of 4f- orbitals whereas actinoids are involved in the filling of 5f-orbitals. The binding energy of 4f electrons is comparatively less than that of 5f-electrons. The shielding effect of 5f-electrons is less effective as compared to that of 4f-electrons.
- The paramagnetic properties of lanthanoids can be easily explained but this explanation is difficult in case of actinoids.
- Lanthanides are non-radioactive in nature except promethium whereas all actinide series elements are radioactive.
- Lanthanides do not have a tendency to form oxo-cations, but several oxo-cations of actinide series exist. The compounds formed by lanthanides are less basic on the other hand the compounds of actinides are highly basic.

Similarities between Lanthanides and Actinides:

The elements of lanthanide and actinide series are characterized by filling of (n-2) f subshell. They possess almost similar outermost electronic configuration hence have similar properties. Following are the significant similarities:

1. Both have a prominent oxidation state of +3.
2. They are involved in the filling of (n-2) f orbitals.
3. They are highly electropositive and very reactive in nature.
4. With an increase in atomic number, there is a decrease in atomic and ionic size.
5. Both show magnetic properties.

Chemical Reactivity of Lanthanides:

All the lanthanides show similarity in the reactivity but are greater than the transition elements. This is due to the shielding of unpaired electrons of the inner 4f-orbital by the outer 5s, 5p, and 5d orbital's.

Get readily tarnished with oxygen and forms the oxides of M2O3 except for CeO2 which reacts with hydrogen forming solid hydrides at 300-400 C.

Hydrides get decomposed by water. Halides can be made by heating metal with halogen or the oxide with ammonium halide. Chlorides are deliquescent while fluorides are insoluble. Nitrates, acetates, sulphates are soluble while carbonate, phosphate, chromates and oxalates are insoluble in water.

Ionization Energy of Lanthanides

Ionization energy is the energy ne eded to remove the valence electron from the atom/ion and is directly related to the force of attraction on the electron. Hence larger the nuclear charge and smaller the radii of the electron larger will be the ionization energy (IE). Also, the ionization energy will be more for half-filled and fully filled orbitals.

IE of the lanthanides elements is larger than s-block and smaller than the d block elements, between which, they are placed.

Physical Properties of Lanthanides:

1. Density: Density being the ratio of the mass of the substance to its volume, density of d-block elements will be more than the s-block elements. Among the inner transition series, the trend in density will be reverse of atomic radii, ie. density increases, with an increasing atomic number along the period.

They have a high density ranging between 6.77 to 9.74 g cm-3. It increases with increasing atomic number.

2. Melting and Boiling Points: They have a fairly high melting point but there is no definite trend in the melting and boiling point of lanthanides.

3. Magnetic Properties: Materials are classified by their interaction with the magnetic field as:

- Diamagnetic if repelled
- Paramagnetic if attracted

The lanthanide atoms/ions other than f0 and f14 type are paramagnetic in nature due to unpaired electrons in orbitals. Hence Lu^{3+}, Yb^{2+} and Ce^{4+} are diamagnetic.

Unpaired electrons contribute to 'orbital magnetic moment' and 'spin magnetic moment'. Orbital angular moment and spin magnetic moment of the electrons are taken into account for calculating the total magnetic moment.
$M = \sqrt{[4S(S+1)+L(L+1)]}$ BM and its unit is Bohr Magneton (BM)

Formation of Coloured Ions

Lanthanides ions can have electrons in f-orbital and also empty orbitals like the d-block elements. When a frequency of light is absorbed, the light transmitted exhibit a colour complementary to the frequency absorbed. Inner transition element ions can absorb the frequency in the visible region to use it for f-f electron transition and produce visible colour.

Many of the lanthanide metals are silver-white. The lanthanide ions with +3 oxidation state are coloured both in solid-state and in aqueous solution.

The colour of a cation depends on the number of unpaired f electrons Lanthanides, with xf electrons, have the same colour as of (14-x) electron elements.

Uses of Lanthanides:

- **Metallurgical applications**: Some of the alloys of lanthanide elements find important metallurgical applications as reducing agents. Example: Misch metals (Ce- 30 to 35%)

- **Ceramic applications**: Ce(III) and Ce(IV) oxides find use in glass polishing powders whereas Nd and Pr oxides are extensively used in colouring glass and in the production of standard light filters.
- **Catalytic applications**: Some lanthanide compounds are used as catalysts. Example: Cerium phosphate is used in petroleum cracking as a catalyst.
- **Electronic applications**: The ferromagnetic garnets of 3Ln2O3.5Fe2O3 type are used in microwave devices.
- **Nuclear applications**: These elements and some of their compounds are used in nuclear control devices, shielding devices and fluxing devices. Sm – 140, Eu – 153, Gd- 155, Gd-157 and Dy- 164 are some of the important isotopes used in nuclear technology.
- Oxides of lanthanides are useful as phosphors in fluorescent materials.
- Ceramic sulphate is a good analytical oxidizing agent.

Extraction ofThorium:

- **Thorium** is a weakly radioactive metallic chemical element with the symbol **Th** and atomic number 90. Thorium is silvery and tarnishes black when it is exposed to air, forming thorium dioxide; it is moderately hard, malleable, and has a high melting point. Thorium is an electropositive actinide whose chemistry is dominated by the +4 oxidation state; it is quite reactive and can ignite in air when finely divided.

Production:

- The low demand makes working mines for extraction of thorium alone not profitable, and it is almost always extracted with the rare earths, which themselves may be by-products of production of other minerals.

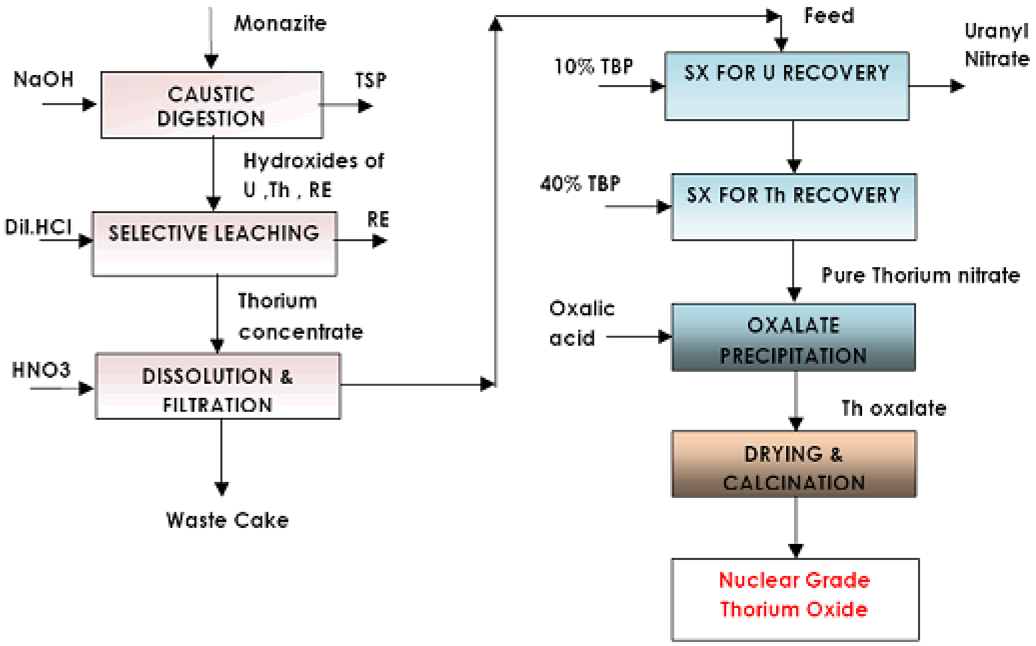
- The current reliance on monazite for production is due to thorium being largely produced as a by-product; other sources such as thorite contain more thorium and could easily be used for production if demand rose.

The common production route of thorium constitutes concentration of thorium minerals; extraction of thorium from the concentrate; purification of thorium; and (optionally) conversion to compounds, such as thorium dioxide.

Concentration:

There are two categories of thorium minerals for thorium extraction: primary and secondary. Primary deposits occur in acidic granitic magmas and pegmatites. They are concentrated, but of small size. Secondary deposits occur at the mouths of rivers in granitic mountain regions. In these deposits, thorium is enriched along with other heavy minerals. Initial concentration varies with the type of deposit.

For the primary deposits, the source pegmatites, which are usually obtained by mining, are divided into small parts and then undergo flotation. Alkaline earth metal carbonates may be removed after reaction with hydrogen chloride; then follow thickening, filtration, and calcination. The result is a concentrate with rare-earth content of up to 90%.Secondary materials (such as coastal sands) undergo gravity separation. Magnetic separation follows, with a series of magnets of increasing strength. Monazite obtained by this method can be as pure as 98%.



Concept of Acids, Bases:

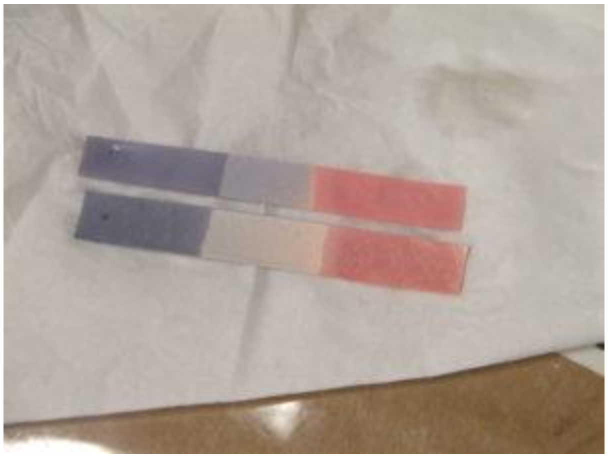
Acids:

Acidity is a characteristic property of acids. Acidic substances are usually very sour. Apart from hydrochloric acid, there are many other types of acids around us. Citrus fruits like lemons and oranges contain citric and ascorbic acids while tamarind paste contains tartaric acid.

In fact, the word ‘acid’ and ‘acidity’ are derived from the Latin word ‘acidus’ which means sour. If you dip a blue litmus paper into an acid, it will turn red while a red litmus paper will not change colour. Acids also liberate dihydrogen when they react with some metals.

Bases:

Bases turn red litmus paper blue while the blue litmus paper stays blue. They taste bitter and also feel soapy. Some other common examples of bases include sodium bicarbonate that is used in cooking and household bleach.



The three most important modern concepts of acids and bases are:

Arrhenius Concept:

According to Arrhenius concept, Substances which produce **H^+ ions** when dissolved in water are called acids while those which ionize in water to produce **OH^- ions** are called bases.

$$HA \rightarrow H^+ + A^- \text{ (Acid)}$$

$$BOH \rightarrow B^+ + OH^- \text{ (Base)}$$

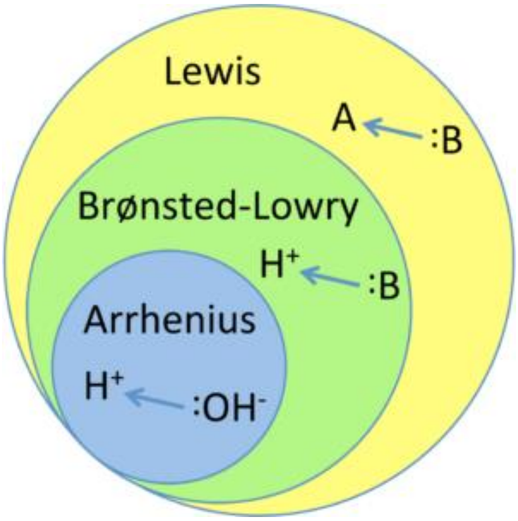
Arrhenius proposed that acid-base reactions are characterized by acids if they dissociate in aqueous solution to form hydrogen ions (H^+) and bases if they form hydroxide (OH^-) ions in aqueous solution.

Limitations of Arrhenius Concept:

- The presence of water is absolutely necessary for acids and bases. Dry HCl can't act as an acid. HCl acts as an acid in water only and not any other solvent.
- The concept does not explain the acidic and basic character of substances in non-aqueous solvents.
- The neutralization process is only possible for reactions which can occur in aqueous solutions, although reactions involving salt formation can occur in the absence of a solvent.
- The acidic character of some salts such as $AlCl_3$ in aqueous solution can't be explained.
- An extended as well as artificial explanation is needed to define the basic nature of NH_3.

Bronsted-Lowry Concept:

Bronsted and Lowry in 1923 independently proposed a more general definition of acids and bases. According to them, an acid is defined as any hydrogen-containing material (molecule, anion or cation) which can donate a proton to other substance and a Base is any substance(molecule, cation or anion) that can accept a proton from any other substance. Therefore, acids are proton donor whereas bases are proton acceptor.



Conjugate Acid-Base Pairs

Consider a reaction

$$\text{Acid}_1 + \text{Base}_2 \rightarrow \text{Acid}_2 + \text{Base}_1$$

$$H_2O + HCl \Leftrightarrow H_3O^+ + Cl^-$$

In this reaction, HCl donates a proton to H_2O and is, therefore an acid. Water, on the other hand, accepts a proton from HCl, and is, therefore, a base. In the reverse reaction which at equilibrium proceeds at the same rate as the forward reaction, the H_3O^+ ions donate a proton to Cl– ion, hence H_3O^+, an ion is an acid. Cl^- ion, because it accepts a proton fromH_3O^+ ion, is a base.

Acid-base pairs in which the members of reaction can be formed from each other by the gain or loss of protons are called conjugate acid-base pairs.

Limitations of Bronsted Lowry Concept:

- Bronsted Lowry could not explain the reaction occurring in the non-protonic solvent like $COCl_3$, SO_2, N_2O_4, etc.
- It cannot explain the reactions between acidic oxides like etc and the basic oxides like etc which can easily take place in the absence of solvent as well e.g. (No proton transfer)
- Substances like BF_3, $AlCl_3$ etc, do not contain hydrogen which means they can't donate a proton, still they behave as acids.

Lewis Concept:

According to Lewis theory of acid-base reactions, bases donate pairs of electrons and acids accept pairs of electrons. Thus, it can be said that a Lewis acid is electron-pair acceptor.

The advantage of the Lewis theory is that complements the model of oxidation-reduction reactions. Oxidation-reduction reactions take place on a transfer of electrons from one atom to another, with a net change in the oxidation number of one or more atoms.

The Lewis theory further suggested that acids react with bases and share a pair of electrons but there is no change in the oxidation numbers of any atoms. Either an electron is transferred from one atom to another, or the atoms come together to share a pair of electrons.

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \text{ (Aluminium hydroxide is acting as a base)}$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)^{4-} \text{ (Aluminium hydroxide is acting as an acid)}$$

These reactions are showing clearly: When Aluminium hydroxide accepts protons, it acts as a base. When it accepts electrons, it acts as an acid. This Lewis acid-base theory also explains why non-metal oxides such as carbon dioxide dissolve in H_2O to form acids, such as carbonic acid H_2CO_3.

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Limitations of Lewis Concept:

- Lewis concept gave a generalized idea including all coordination reactions and compounds. This is not true always.
- An idea about the relative strength of acids and bases is not provided by Lewis concept.
- Lewis concept is not in line with the acid-base reaction concept.
- Lewis concept has not discussed the behaviour of protonic acids like HCl.

Solved Example for You:

Question: Whether the following ions or molecules can act as Lewis acid or a Lewis base?

- Ag^+
- NH_3

Solution:

- A silver cation is Lewis acid.
- Ammonia is Lewis base.

UNIT II

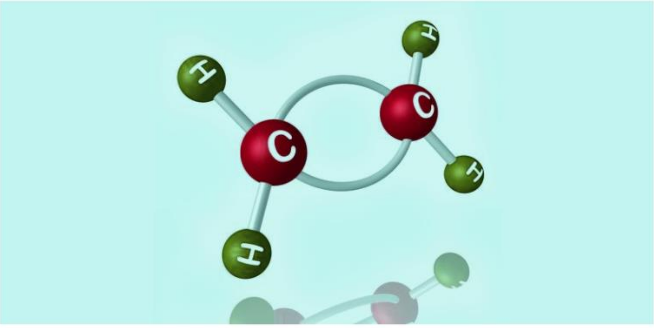
CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

Introduction:

Organometallic Compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule. Even metalloid elements such as silicon, tin, and boron are known to form organometallic compounds which are used in some industrial chemical reactions.

The catalysis of reactions wherein the target molecules are polymers or pharmaceuticals can be done with the help of organometallic compounds, resulting in an increase in the rate of the reactions.

Generally, the bond between the metal atom and the carbon belonging to the organic compound is covalent in nature. When metals with relatively high electropositivity (such as sodium and lithium) form these compounds, a carbanionic nature is exhibited by the carbon which is bound to the central metal atom.



An example of an organometallic compound wherein carbons belonging to a benzene molecule bond with chromium is illustrated above. A few more examples of these types of compounds are Grignard reagents, tetracarbonyl nickel, and dimethyl magnesium.

Preparation of Organomagnesium Compounds:

The general the synthesis of a Grignard reagent involves the reaction of an alkyl halide (RX, where X = Cl, Br, I) with magnesium metal in a suitable ether solvent, Equation.

$$RX + Mg \rightarrow RMgX$$

While diethyl ether (Et_2O) and tetrahydrofuran (THF) are commonly used as solvents, other polar non-protic solvents are suitable, including: triethylamine (NEt_3), dimethylsulphide (Me_2S), dimethylselenide (Me_2Se), and dimethyltelluride (Me_2Te).

The relative order of reactivity of the alkyl halide follows the trend:

$$I > Br > Cl > F$$

In fact alkyl fluorides are sufficiently inert that highly coordinating polar solvents such as THF or dimethylformamide (DMF) must be used.

If the reaction is allowed to get too hot then several possible side reactions can occur. In THF reaction with the solvent occurs:

$$RMgX + THF \rightarrow RH + H_2C{=}CH_2 + H_2C{=}C(H)MgX$$

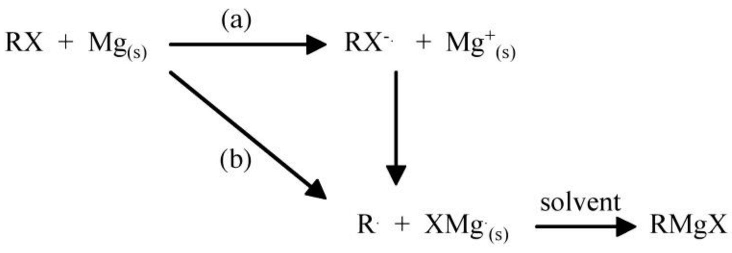
Alternatively, a transition metal catalyzed radical coupling between the Grignard and unreacted alkyl halide is observed irrespective of the identity of the solvent, Equation.

$$RMgX + RX \rightarrow R\text{-}R + MgX_2$$

The mechanism for Grignard formation is thought to be radical in nature; however, a study of the surface of the magnesium during the reaction has shown the presence of corrosion pits. It is generally agreed that initiation occurs at surface dislocations, but the major reaction occurs at a polished surface.

The kinetics of the reaction is 1st order with respect to the alkyl halide concentration, but it has also been claimed to be 1st order with respect to the solvent concentration. It has therefore been concluded that the rate-determining step involves the metal solvent interface.

The reaction of magnesium with aryl bromides has been studied and is proposed to occur by two reactions. The first involves electron transfer between the aryl halide and the metal, while the second involves aryl radical formation.



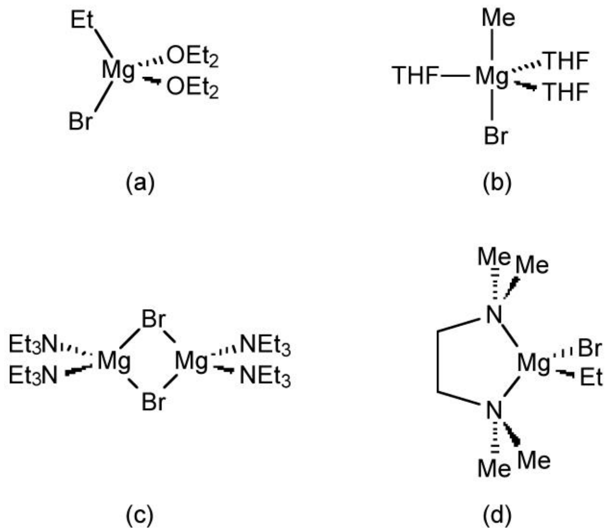
A number of alternative synthetic routes are used with polyhalogenated hydrocarbons, Equation and Equation, and where the alkyl radical is unstable, Equation.

$$X_3CH + {}^{i}PrMgX \rightarrow (X_3C)MgX + {}^{i}PrH$$

C_6Br_6 + EtMgX → (C_6Br_5)MgX + EtBr

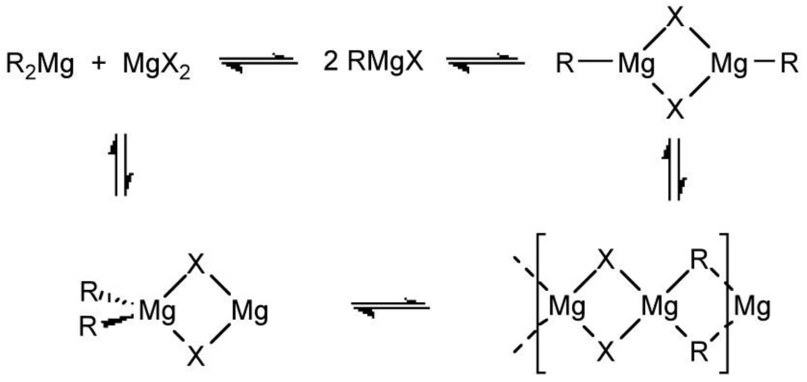
RX + R'MgX' → RMgX' + R'X

The solid state structure of Grignard reagents is controlled by the presence and identity of the solvent used in the synthesis. In this regard the size and the basicity of the solvent is important. For example, the structure of EtMgBr crystallized from diethyl ether exists as a 4-ccordinate monomer (Figurea), while the use of the sterically less demanding THF results in a 5-coordinate monomeric structure (Figureb). In contrast, the use of triethylamine yields a dimeric bromide bridged structure (Figurec), and the use of a chelate bidentate amine gives a structure (Figured) similar to that observed with diethyl ether (Figurea).



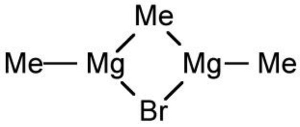
Molecular structure of EtMgBr in (a) diethyl ether, (b) THF, (c) triethyl amine, and (d) tetramethyletheylenediamine (TMED).

In solution, Grignards are fluxional such that no single defined structure is present. The series of exchange reactions are known as an extended Schlenk equilibrium (Figure).



Schematic representation of the extended Schlenk equilibrium observed for Grignard compounds in solution.

It is observed that Grignard solutions are also slightly conducting, and magnesium is deposited at both the anode and cathode suggesting the formation of RMg^+ and $[RMgX_2]^-$. The alkyl/halide exchange is thought to occur through a bridging intermediate (Figure).



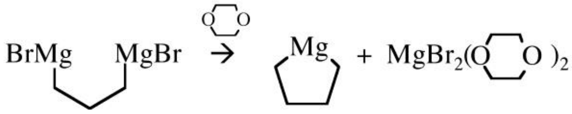
Dialkyl magnesium (R_2Mg)

Dialkyl magnesium compounds are involatile white solids. They generally have similar reactivity to their Grignard analogs.

Synthesis

The most common synthesis of R_2Mg is by the reaction of a Grignard with dioxane ($C_4H_8O_2$), Equation, where the precipitation of the dihalide is the reaction driving force.

This method is useful for the synthesis of cyclic compounds, Equation.



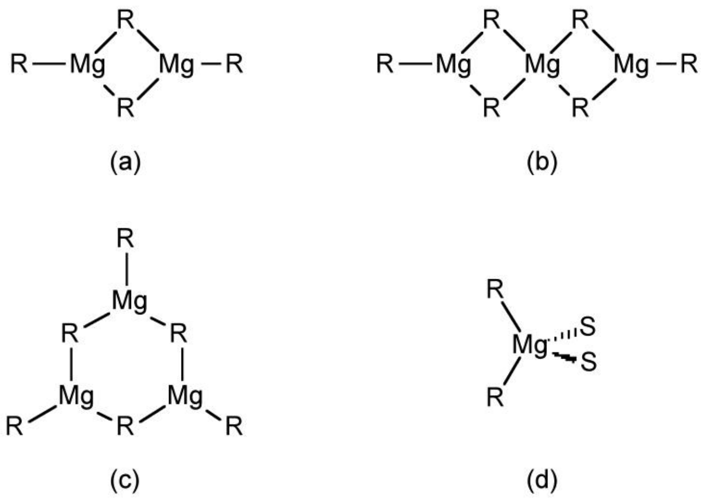
An alternative synthesis that does not require dioxane involves the metal exchange reaction between magnesium metal and a dialkyl mercury compound.

$$R_2Hg + Mg \rightarrow R_2Mg + Hg$$

Finally, in selected cases, magnesium will react with acidic hydrocarbons such as cyclopentadienyl at high temperatures (600 °C).

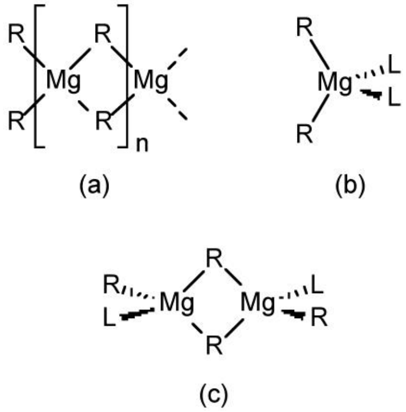
Structure

In the vapor phase dialkyl magnesium compounds are generally monomeric linear compounds. In solution, in the absence of coordinating solvents R_2Mg form a variety of oligomers (Figurea-c) in solution as determined by molecular weight measurements. In the presence of coordinating solvents 4-coordinate monomers predominate (Figured).



Solution structure of R_2Mg (R = Me, Et) in (a – c) non-coordinating solvents, and (d) diethyl ether.

As similar trend is observed in the solid state, where polymers have been characterized in the absence of coordinating solvents (Figurea), while monomers or dimmers are generally observed when crystallized from a coordinating solvent (Figureb and c).



Solid state structure of R_2Mg (R = Me, Et) crystallized in (a) the absence and (b and c) the presence of a coordinating solvents.

Poperties:

Hydrolysis and related reactions

Grignard compounds react with water to give the hydrocarbon, Equation, they also react with other hydroxylic compounds such as alcohols and carboxylic acids. One important use of the hydrolysis reaction is specifically deuteration, Equation.

Equation.

$$CH_3MgBr + H_2O \rightarrow CH_4 + BrMgOH$$

$$CH_3CH_2(CH_3)_2CMgBr + D_2O \rightarrow CH_3CH_2(CH_3)_2CD + BrMgOD$$

The hydrogen atom on a terminal alkyne is sufficiently acidic that the reaction with Grignards occurs in an analogous manner to that of hydrolysis.

$$C_6H_5C{\equiv}CH + C_2H_5MgBr \rightarrow C_6H_5C{\equiv}CMgBr + C_2H_6$$

Once formed the alkynyl Grignard undergoes the same hydrolysis reaction.

$$C_6H_5C{\equiv}CMgBr + D_2O \rightarrow C_6H_5C{\equiv}CD + BrMgOD$$

Reaction with CO_2

Grignards react readily with carbon dioxide to form the carboxylate, which yields the associated carboxylic acid upon hydrolysis, Equation.

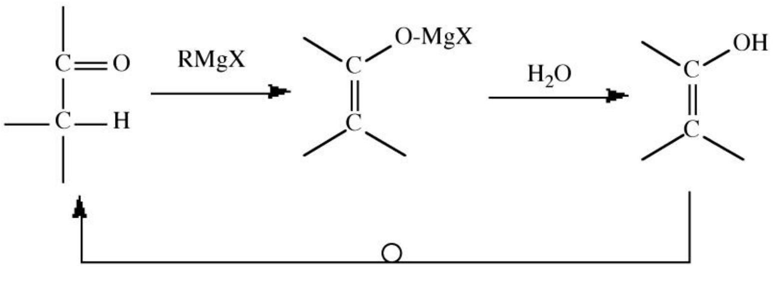
$$RMgX + CO_2 \rightarrow RCO_2MgX \xrightarrow{H_2O} RCO_2H + HOMgX$$

Reaction with carbonyls

Organomagnesium compounds react with organic carbonyls (aldehydes, ketones, and esters) to yield the alcohol on hydrolysis, Equation. This synthetic route is useful for the formation of primary, secondary and terminal alcohols.

$$RMgX + R'_2C{=}O \rightarrow R'_2(R)COMgX \xrightarrow{H_2O} R'_2(R)COH + HOMgX$$

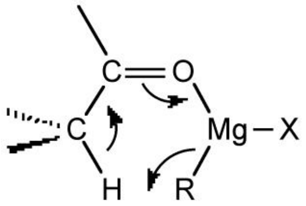
Unfortunately, for some carbonyls there is a competing side reaction of enolization, where the starting ketone is reformed upon hydrolysis.



When the Grignard reagent has a β-hydrogen another side reaction occurs in which the carbonyl group is reduced and an alkene is formed.

$$R_2C{=}O + (CH_3CH_2)MgX \rightarrow R_2(H)COH + H_2C{=}CH_2$$

Both the enolization and reduction occur via similar 6-membered cyclic transition states (Figure).



Representation of the 6-membered transition state reaction for enolization of a ketone.

Grignards react with α,β-unsaturated ketones to give either the 1,2-addition product or the 1,4-addition product, or both.

$$Ph(H)C{=}C(H){-}C(O)Me + EtMgBr \xrightarrow{H_2O} \begin{array}{c} Ph(H)C{=}C(H){-}C(OH)EtMe \\ + \\ Ph(H)EtC{-}CH_2{-}C(O)Me \end{array}$$

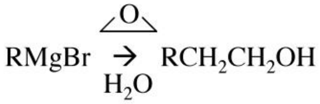
Reaction with acyl halides

Acyl halides react with Grignards to give ketones, Equation. Best results are obtained if the reaction is carried out at low temperature and in the presence of a Lewis acid catalysts (e.g., $FeCl_3$).

$$CH_3C(O)Cl + RMgX \rightarrow CH_3C(O)R + XMgCl$$

Reaction with epoxides

Oxirane (epoxide) rings are opened by Grignards, Equation, in a useful reaction that extends the carbon chain of the Grignard by two carbon atoms. This reaction is best performed with ethylene oxide since the magnesium halide formed is a Lewis acid catalyst for further reactions in the case of substituted oxiranes.



$$RMgBr \xrightarrow[H_2O]{O} RCH_2CH_2OH$$

Reaction with salts

One of the most useful methods of preparing organometallic compounds is the exchange reaction of one organometallic compound with a salt of a different metal, Equation. This is an equilibrium process, whose equilibrium constant is defined by the reduction potential of both metals. In general the reaction will proceed so that the more electropositive metal will form the more ionic salt (usually chloride).

$$RM + M'X \rightleftharpoons RM' + MX$$

Grignard reagents are particularly useful in this regard, and may be used to prepare a wide range of organometallic compounds. For example:

$$2\ CH_3CH_2MgCl + CdCl_2 \rightarrow Cd(CH_2CH_3)_2 + 2\ MgCl_2$$

$$4\ CH_3MgCl + SiCl_4 \rightarrow Si(CH_3)_4 + 4\ MgCl_2$$

The reaction with a Grignard is milder than the analogous reaction with lithium reagents, and leads to a lower incident of side-products.

Organozinc compound

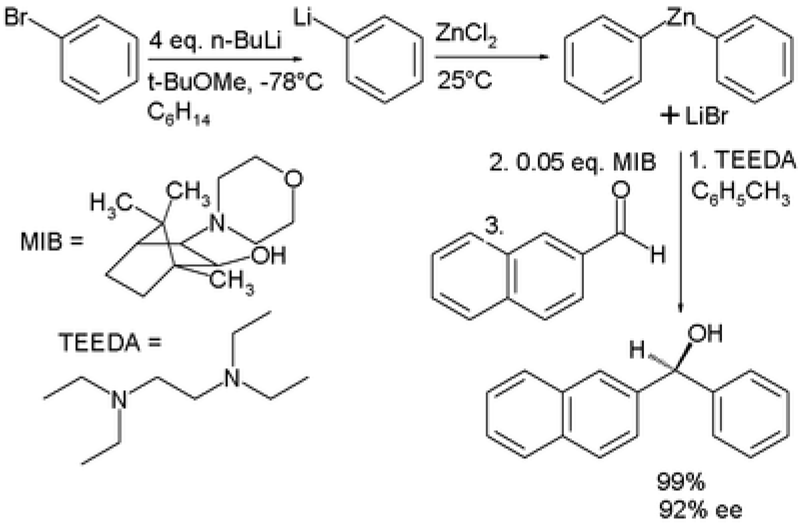
Organozinc compounds in organic chemistry contain carbon to zinc chemical bonds. **Organozinc chemistry** is the science of organozinc compounds describing their physical properties, synthesis and reactions

Organozincs can be categorized according to the number of carbon substituents that are bound to the metal.

1. Diorganozinc (R_2Zn): A class of organozinc compounds in which two alkyl ligands. These may be further divided into subclasses depending on the other ligands attached
2. Heteroleptic (RZnX): Compounds which an electronegative or monoanionic ligand (X), such as a halide, is attached to the zinc center with another alkyl or aryl substituent (R).
3. Ionic organozinc compounds: This class is divided into organozincates (R_nZn^-) and organozinc cations ($RZnL_n^+$).

Preparation:

Several methods exist for the generation of organozinc compounds. Commercially available diorganozinc compounds are dimethylzinc, diethylzinc and diphenylzinc. These reagents are expensive and difficult to handle. In one study the active organozinc compound is obtained from much cheaper organobromine precursors:

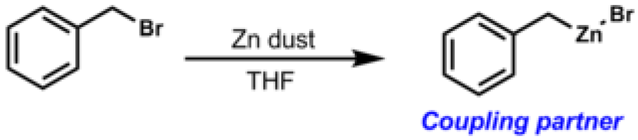


From zinc metal

Frankland's original synthesis of diethylzinc involves the reaction of ethyl iodide with zinc metal. The zinc must be activated to facilitate this redox reaction. One of such activated form of zinc employed by Frankland is zinc-copper couple.

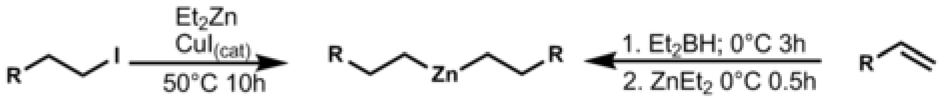
$2EtI+2Zn^0 \rightarrow Et_2Zn+ZnI_2$

Riecke zinc, produced by in situ reduction of $ZnCl_2$ with potassium, is another activated form of zinc. This form has proven useful for reactions such as Negishi coupling and Fukuyama coupling. Formation of organozinc reagents is facilitated for alkyl or aryl halides bearing electron-withdrawing substituents, e.g., nitriles and esters.

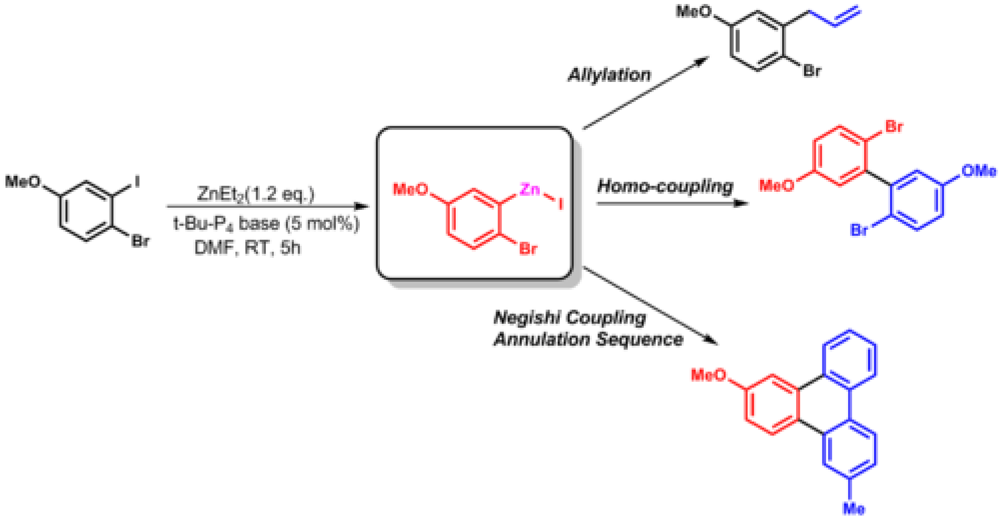


Functional group exchange

The two most common zinc functional group interconversion reactions are with halides and boron, which is catalyzed by copper iodide (CuI) or base. The boron intermediate is synthesized by an initial hydroboration reaction followed by treatment with diethyl zinc. This synthesis shows the utility of organozinc reagents by displaying high selectivity for the most reactive site in the molecule, as well as creating useful coupling partners.[12]



This group transfer reaction can be used in allylation, or other coupling reactions (such as Negishi coupling).[13]



β-Silyl diorganozinc compounds

One of the major drawbacks of diorganozinc alkylations is that only one of the two alkyl substituents is transferred. This problem can be solved by using Me_3SiCH_2- (TMSM), which is a non-transferable group.

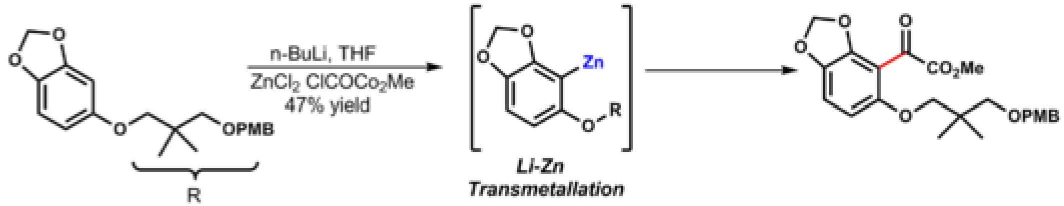
Transmetallation

Transmetallation is similar to the interconversions displayed above zinc can exchange with other metals such as mercury, lithium, copper, etc. One example of this reaction is the reaction of diphenylmercury with zinc metal to form diphenylzinc and metallic mercury:

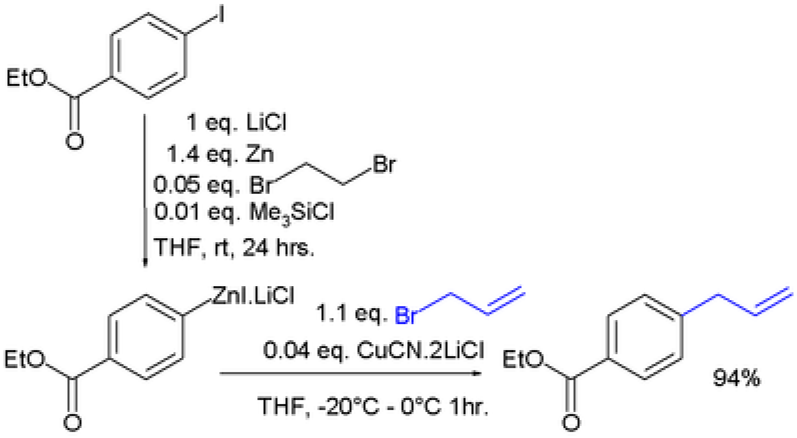
$HgPh_2 + Zn \rightarrow ZnPh_2 + Hg$

The benefit of transmetalling to zinc it is often more tolerant of other functional groups in the molecule due to the low reactivity which increases selectivity.

- In the synthesis of Maoecrystal V, a directed ortho metalation gives the initial aryl-lithium species, which is transmetallated to the desired arylzinc compound. The arylzinc compound is significantly less reactive than the aryl-lithium species and thus better tolerates the functionality in the subsequent coupling with methyl chlorooxaloacetate. Esters are significantly stable against organozinc reagents.



Organozinc can be obtained directly from zinc metal:



In this method zinc is activated by 1,2-dibromoethane and trimethylsilyl chloride. A key ingredient is lithium chloride which quickly forms a soluble adduct with the organozinc compound thus removing it from the metal surface.

Reactions

In many of their reactions organozincs appear as intermediates.

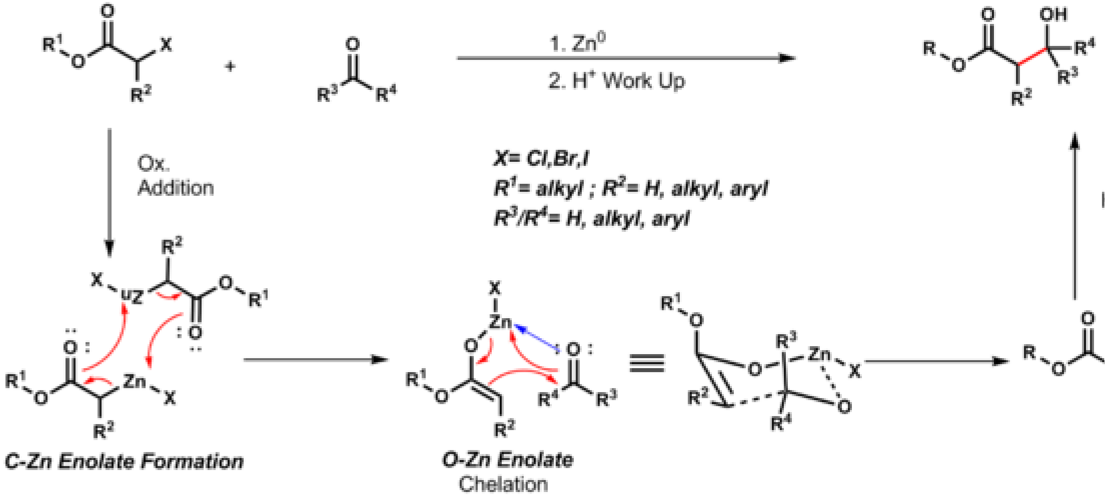
- In the **Frankland–Duppa reaction** (1863) an oxalate ester (ROCOCOOR) reacts with an alkyl halide R'X, zinc and hydrochloric acid to the α-hydroxycarboxylic esters RR'COHCOOR[19]

Reformatsky reaction

This organic reaction can be employed to convert α-haloester and ketone or aldehyde to a β-hydroxyester. Acid is needed to protonate the resulting alkoxide during work up. The initial step is an oxidative addition of zinc metal into the carbon-halogen bond, thus forming a carbon-zinc enolate. This C-Zn enolate can then rearrange to the Oxygen-Zinc enolate via coordination. Once this is formed the other carbonyl containing starting material will coordinate in the manner shown below and give the product after protonation. The benefits of the Reformatsky reaction over the conventional aldol reaction protocols is the following:

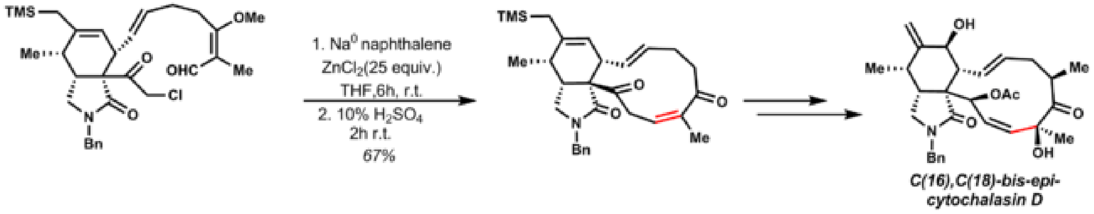
1. Allows for exceedingly derivatized ketone substrates
2. The ester enolate intermediate can be formed in the presence of enolizable moieties
3. Well suited for intramolecular reactions

Below shows the six-membered transition state of the Zimmerman–Traxler model (Chelation Control, see Aldol reaction), in which R^3 is smaller than R^4.[21]

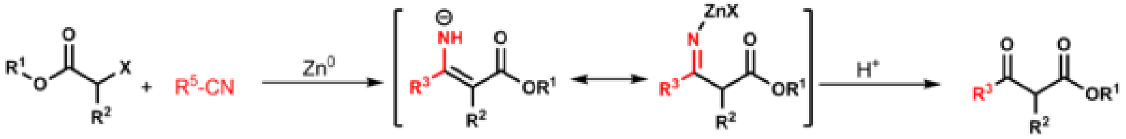


(3.1
)

The Reformatsky reaction has been employed in numerous total syntheses such as the synthesis of C(16),C(18)-bis-epi-cytochalasin D:



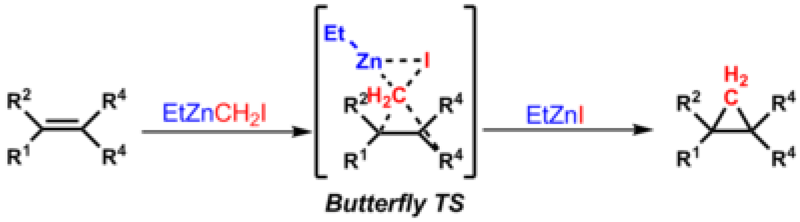
The Reformatsky reaction even allows for with zinc homo-enolates. A modification of the Reformatsky reaction is the Blaise reaction.[21]



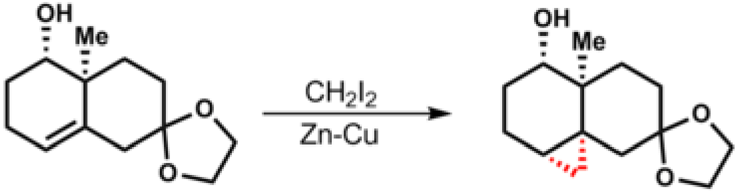
Simmons–Smith reaction

The Simmons–Smith reagent is used to prepare cyclopropanes from olefin using methylene iodide as the methylene source. The reaction is effected with zinc. The key zinc-intermediate formed is a carbenoid (iodomethyl)zinc iodide which reacts with alkenes to afford the cyclopropanated product. The rate of forming the active zinc species is increased via ultrasonication since the initial reaction occurs at the surface of the metal.

(3.4)



Although the mechanism has not been fully elaborated it is hypothesized that the organozinc intermediate is a metal-carbenoid. The intermediate is believed to be a three-centered "butterfly-type". This intermediate can be directed by substituents, such as alcohols, to deliver the cyclopropane on the same side of the molecule. Zinc-copper couple is commonly used to activate zinc.[21]



Organolithium compound:

The alkali metals (Li, Na, K etc.) and the alkaline earth metals (Mg and Ca, together with Zn) are good reducing agents, the former being stronger than the latter. These same metals reduce the carbon-halogen bonds of alkyl halides. The halogen is converted to a halide anion, and the carbon bonds to the metal which has characteristics similar to a carbanion (R:-).

Formation

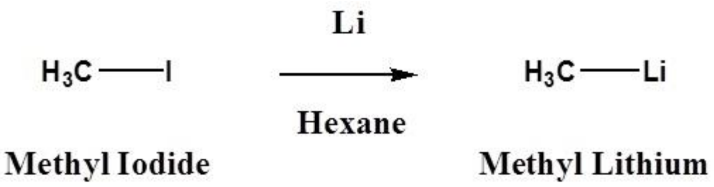
- **An Alkyl Lithium Reagent**

$R_3C-X+2Li \rightarrow R_3C-Li+LiX$(1)

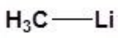
- **A Grignard Regent**

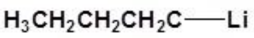
$R_3C-X+Mg \rightarrow R_3C-MgX$(2)

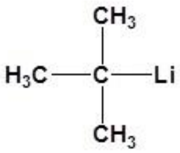
Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used. The alkyl magnesium halides described in the second reaction are called Grignard Reagents. Although the formulas drawn here for the alkyl lithium and Grignard reagents reflect the stoichiometry of the reactions and are widely used in the chemical literature, they do not accurately depict the structural nature of these remarkable substances. Mixtures of polymeric and other associated and complexed species are in equilibrium under the conditions normally used for their preparation.

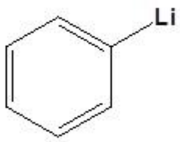


Common Organometallic Reagents


Methyl Lithium

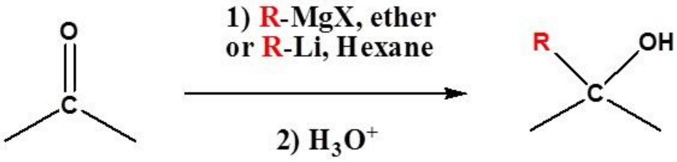

Butyl Lithium


t-Butyl Lithium


Phenyl Lithium

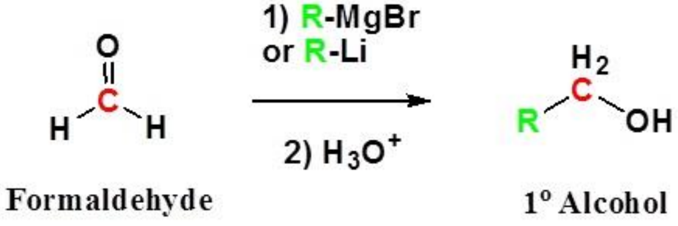
Reaction of Organolithium Reagents with Various Carbonyls

Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.



Both Grignard and Organolithium Reagents will perform these reactions.

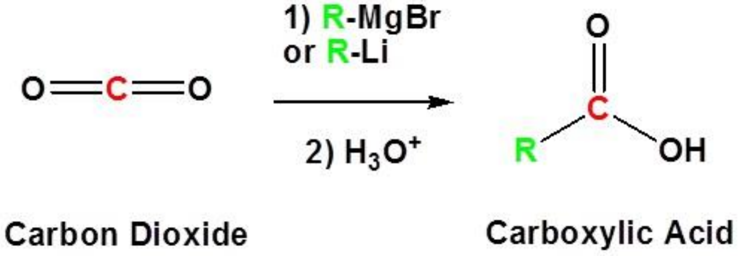
Addition to formaldehyde gives 1° alcohols

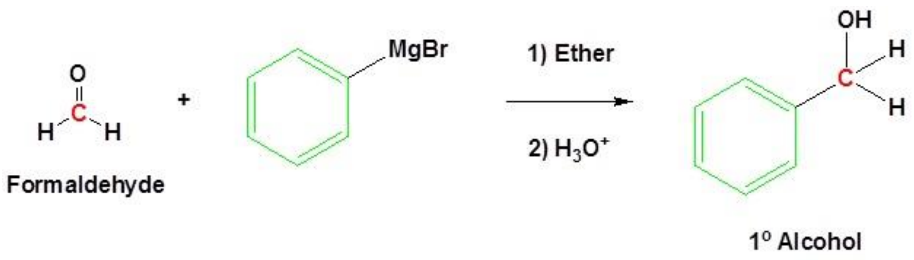


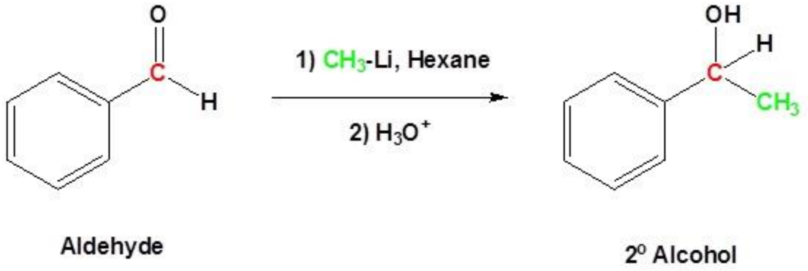
Addition to aldehydes gives 2° alcohols

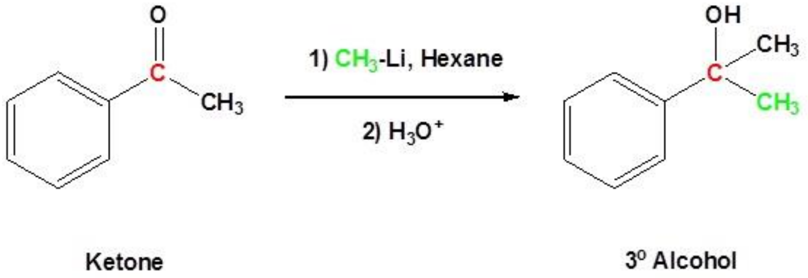
Addition to ketones gives 3° alcohols

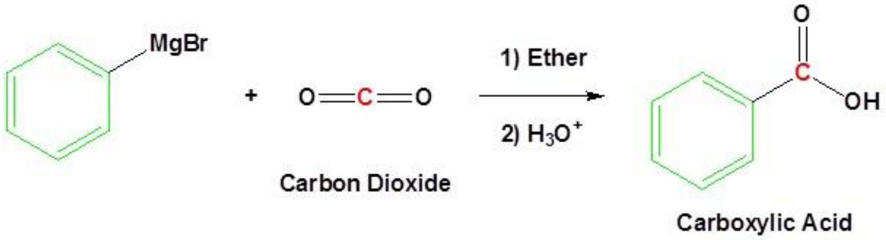
Addition to carbon dioxide (CO_2) forms a carboxylic acid



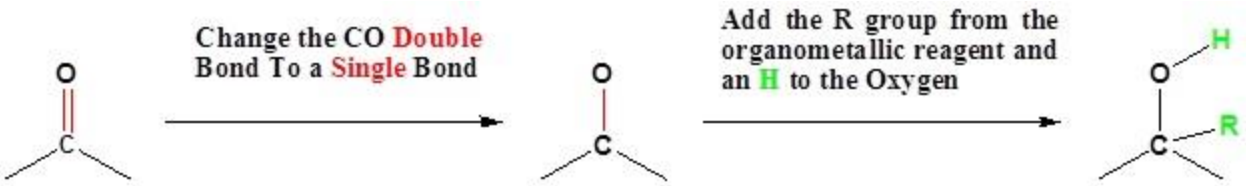








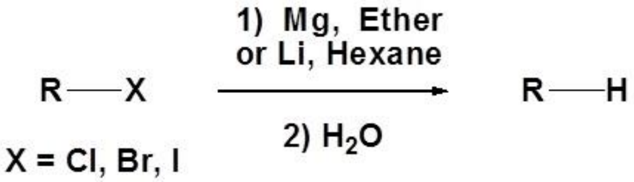
Going from Reactants to Products Simplified



Organometallic Lithium as Bases

These reagents are very strong bases (pKa's of saturated hydrocarbons range from 42 to 50). Although not usually done with Grignard reagents, organolithium reagents can be used as strong bases. Both Grignard reagents and organolithium reagents react with water to form the corresponding hydrocarbon. This is why so much care is needed to insure dry glassware and solvents when working with organometallic reagents.

In fact, the reactivity of Grignard reagents and organolithium reagents can be exploited to create a new method for the conversion of halogens to the corresponding hydrocarbon (illustrated below). The halogen is converted to an organometallic reagent and then subsequently reacted with water to from an alkane.



Organocopper compound:

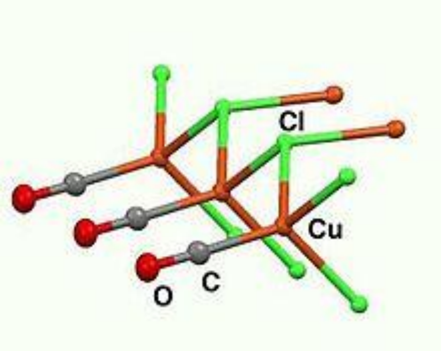
Organocopper compounds in organometallic chemistry contain carbon to copper chemical bonds. **Organocopper chemistry** is the science of organocopper compounds describing their physical properties, synthesis and reactions. They are reagents in organic chemistry.

The first organocopper compound, the explosive copper(I) acetylide Cu_2C_2 (Cu-C≡C-Cu), was synthesized by Rudolf Christian Böttger in 1859 by passing acetylene gas through copper(I) chloride solution:[4]

$$C_2H_2 + 2\ CuCl \rightarrow Cu_2C_2 + 2\ HCl$$

Simple complexes with CO, alkene, and Cp ligands:

Copper(I) salts have long been known to bind CO, albeit weakly. A representative complex is CuCl(CO), which is polymeric. In contrast to classical metal carbonyls, pi-backbonding is not strong in these compounds.



Part of the framework of CuCl(CO). In this coordination polymer, the Cu centers are tetrahedral linked by triply bridging chloride ligands.

Alkenes bind to copper(I), although again generally weakly. The binding of ethylene to Cu in proteins is of broad significance in plant biology so much so that ethylene is classified as a plant hormone. Its presence, detected by the Cu-protein, affects ripening and many other developments.[6]

Although copper does not form a metallocene, half-sandwich complexes can be produced. One such derivative is (η-cyclopentadienyl triethylphosphine) copper.

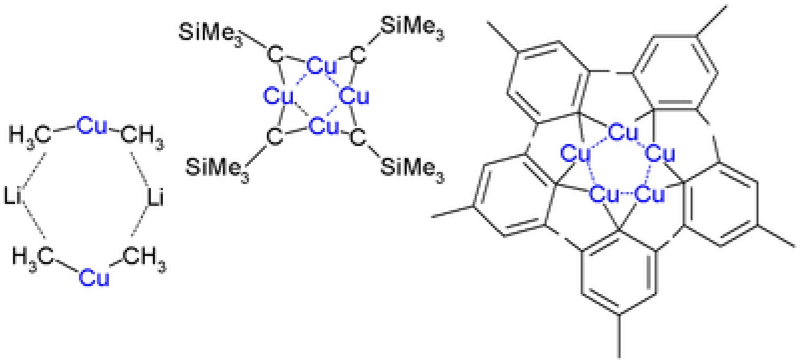
Alkyl and aryl copper(I) compounds

Copper halides react with organolithium reagents to give organocopper compounds. Thus, phenylcopper is prepared by reaction of phenyllithium with copper(I) bromide in diethyl ether. Grignard reagents can be used in place of organolithium compounds. Gilman also investigated the dialkylcuprates. These are obtained by combining two equivalent of RLi with Cu(I) salts. Alternatively, these cuprates are prepared from oligomeric neutral organocopper compounds by treatment with one equivalent of organolithium reagent.

Compounds of the type $[CuR_n]^{(n-1)-}$ are reactive towards oxygen and water, forming copper(I) oxide. They also tend to be thermally unstable, which can be useful in certain coupling reactions. Despite or because of these difficulties, organocopper reagents are frequently generated and consumed in situ with no attempt to isolate them. They are used in organic synthesis as alkylating reagents because they exhibit greater functional group tolerance than corresponding Grignard and organolithium reagents. The electronegativity of copper is much higher than its next-door neighbor in the group 12 elements, zinc, suggesting diminished nucleophilicity for its carbon ligands.

Copper salts react with terminal alkynes to form the acetylides.

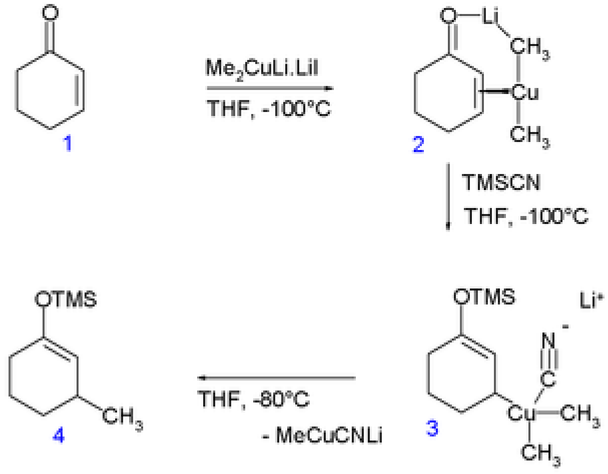
Alkyl halides react with organocopper compounds with inversion of configuration. On the other hand, reactions of organocopper compound with alkenyl halides proceed with retention of subtrate’s configuration.



Lithium dimethylcuprate is a dimer in diethyl ether, forming an 8-membered ring with two lithium atoms linking two methyl groups. Similarly, lithium diphenylcuprate forms a dimeric etherate, $[\{Li(OEt_2)\}(CuPh_2)]_2$, in the solid state.

Alkyl and aryl copper(III) compounds

The involvement of the otherwise rare Cu(III) oxidation state has been demonstrated in the conjugate addition of the Gilman reagent to an enone:[11] In a so-called rapid-injection NMR experiment at -100 °C, the Gilman reagent Me_2CuLi (stabilized by lithium iodide) was introduced to cyclohexenone (**1**) enabling the detection of the copper — alkene pi complex **2**. On subsequent addition of trimethylsilyl cyanide the Cu(III) species **3** is formed (indefinitely stable at that temperature) and on increasing the temperature to -80 °C the conjugate addition product **4**. According to an accompanying in silico experiments [12] the Cu(III) intermediate has a square planar molecular geometry with the cyano group in cis orientation with respect to the cyclohexenyl methine group and anti-parallel to the methine proton. With other ligands than the cyano group this study predicts room temperature stable Cu(III) compounds.



Reactions of organocuprates:

Cross-coupling reactions

Prior to the development of palladium-catalyzed cross coupling reactions, copper was the preferred catalyst for almost a century. Palladium offers a faster, more selective reaction. However, in recent years copper has reemerged as a synthetically useful metal, because of its lower cost and because it is an eco-friendly metal.[13]

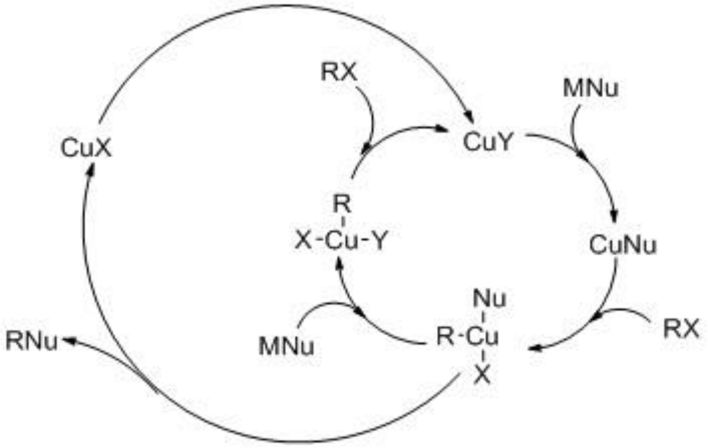
Reactions of R_2CuLi with alkyl halides R'-X give the coupling product:

$R_2CuLi + R'X \rightarrow R\text{-}R' + CuR + LiX$

The reaction mechanism involves oxidative addition (OA) of the alkyl halide to Cu(I), forming a planar Cu(III) intermediate, followed by reductive elimination (RE). The nucleophilic attack is the rate-determining step. In the substitution of iodide, a single-electron transfer mechanism is proposed.

Many electrophiles participate in this reaction. The approximate order of reactivity, beginning with the most reactive, is as follows: acid chlorides> aldehydes > tosylates ~ epoxides > iodides > bromides > chlorides > ketones > esters > nitriles >> alkenes

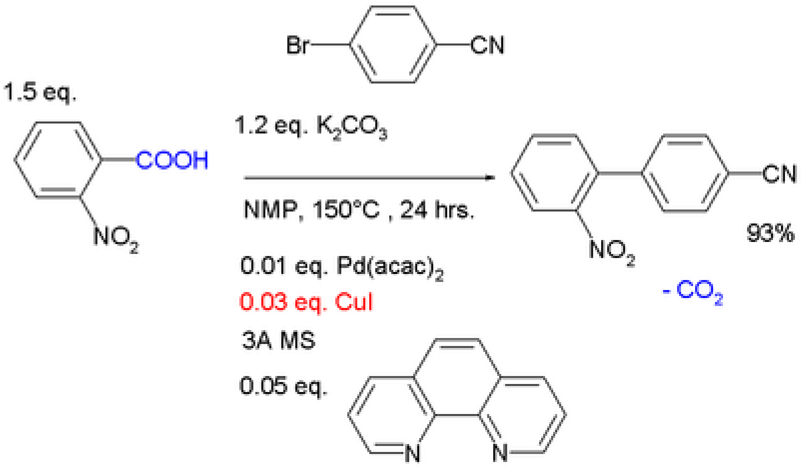
Generally the OA-RE mechanism is analogous to that of palladium-catalyzed cross coupling reactions. One difference between copper and palladium is that copper can undergo single-electron transfer processes.



Coupling reactions

Oxidative coupling is the coupling of copper acetylides to conjugated alkynes in the Glaser coupling (for example in the synthesis of cyclooctadecanonaene) or to aryl halides in the Castro-Stephens Coupling.

Reductive coupling is a coupling reaction of aryl halides with a stoichiometric equivalent of copper metal that occurs in the Ullmann reaction. In an example of a present-day cross coupling reaction called **decarboxylative coupling**, a catalytic amount of Cu(I) displaces a carboxyl group forming the arylcopper (ArCu) intermediate. Simultaneously, a palladium catalyst converts an aryl bromide to the organopalladium intermediate (Ar'PdBr), and on transmetallation the biaryl is formed from ArPdAr'.

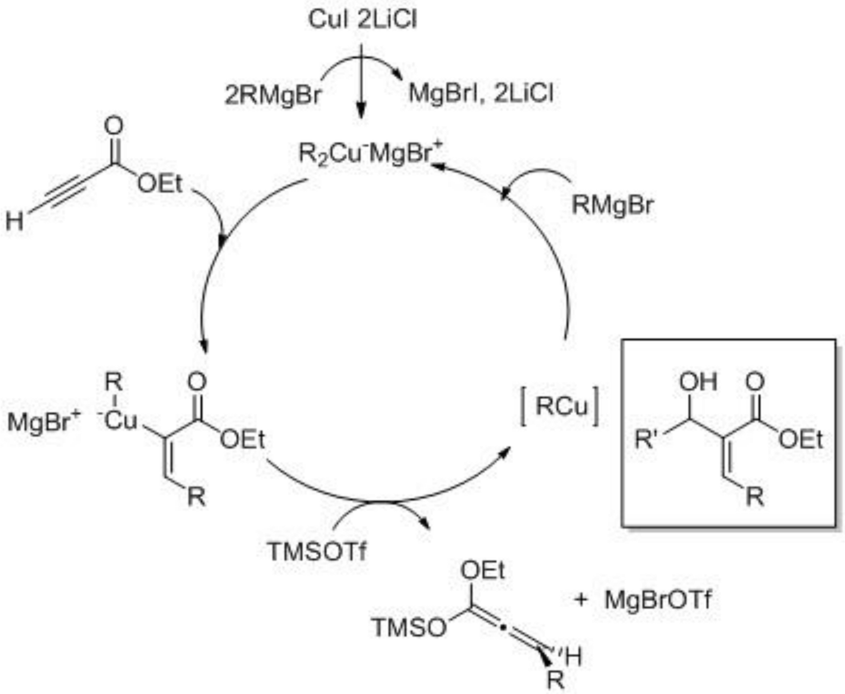


Redox neutral coupling is the coupling of terminal alkynes with halo-alkynes with a copper(I) salt in the Cadiot-Chodkiewicz coupling. Thermal coupling of two organocopper compounds is also possible.

Carbocupration

Carbocupration is a nucleophilic addition of organocopper reagents (R-Cu) to acetylene or terminal alkynes resulting in an alkenylcopper compound (RC=C-Cu). It is a special case of carbometalation and also called the **Normant reaction**.

Figure: Catalytic cycle for carbocupration for the Synthesis of Aldol, Baylis-Hillman Type Products[19]



Synthetic applications

- The Chan-Lam coupling enables the formation of aryl carbon-hetoroatom bonds. It involves coupling of boronic acids, stannanes, or siloxanes with NH- or OH-containing substrates.
- Ullmann reaction involves copper-mediated reactions of aryl halides. Two types of Ullmann reaction are recognized:
- Classic copper-promoted synthesis of symmetric biaryl compounds)
- Copper-promoted nucleophilic aromatic substitution.
- Sonogashira coupling reaction, which utilizes both copper and palladium, entails the coupling of aryl and/or vinyl halides with terminal alkynes.

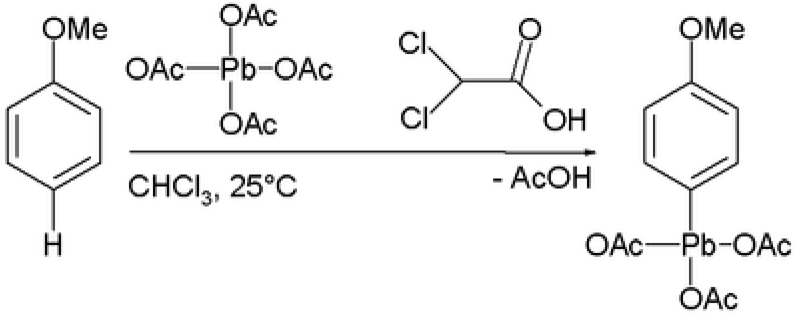
Organolead compound

Organolead compounds are chemical compounds containing a chemical bond between carbon and lead. **Organolead chemistry** is the corresponding science. Sharing the same group with carbon, lead is tetravalent.

Synthesis

Organolead compounds can be derived from Grignard reagents and lead chloride. For example, methylmagnesium chloride reacts with lead chloride to tetramethyllead, a water-clear liquid with boiling point 110 °C and density 1.995 g/cm³. Reaction of a lead(II) source with sodium cyclopentadienide gives the lead metallocene, plumbocene.

Certain arene compounds react directly with lead tetraacetate to aryl lead compounds in an electrophilic aromatic substitution. For instance anisole with lead tetraacetate forms 'p-methoxyphenyllead triacetate in chloroform and dichloroacetic acid:



Other compounds of lead are organolead halides of the type $R_nPbX_{(4-n)}$, organolead sulfinates ($R_nPb(OSOR)_{(4-n)}$) and organolead hydroxides ($R_nPb(OH)_{(4-n)}$). Typical reactions are:

$R_4Pb + HCl \rightarrow R_3PbCl + RH$
$R_4Pb + SO_2 \rightarrow R_3PbO(SO)R$
$R_3PbCl + 1/2Ag_2O\ (aq) \rightarrow R_3PbOH + AgCl$
$R_2PbCl_2 + 2\ OH^- \rightarrow R_2Pb(OH)_2 + 2\ Cl^-$

$R_2Pb(OH)_2$ compounds are amphoteric. At pH lower than 8 they form R_2Pb^{2+} ions and with pH higher than 10, $R_2Pb(OH)_3^-$ ions.

Derived from the hydroxides are the plumboxanes:

$2\ R_3PbOH + Na \rightarrow (R_3Pb)_2O + NaOH + 1/2\ H_2$

which give access to polymeric alkoxides:

$(R_3Pb)_2O + R'OH \rightarrow 1/n\ (R_3PbOR')_n - n\ H_2O$

Reactions

The C–Pb bond is weak and for this reason homolytic cleavage of organolead compounds to free radicals is easy. In its anti-knocking capacity, its purpose is that of a radical initiator. General reaction types of aryl and vinyl organoleads are transmetalation for instance with boronic acids and acid-catalyzed heterocyclic cleavage. Organoleads find use in coupling reactions between arene compounds. They are more reactive than the likewise organotins and can therefore be used to synthesise sterically crowded biaryls.

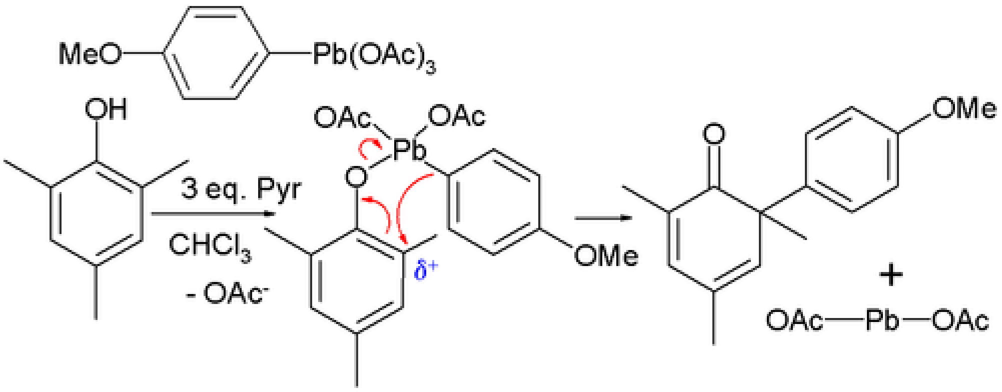
In **oxyplumbation**, organolead alkoxides are added to polar alkenes:

$H_2C{=}CH\text{-}CN + (Et_3PbOMe)_n \rightarrow MeO\text{-}CH_2\text{-}HC(PbEt_3)\text{-}CN \rightarrow MeO\text{-}CH_2\text{-}CH_2\text{-}CN$

The alkoxide is regenerated in the subsequent methanolysis and, therefore, acts as a catalyst.

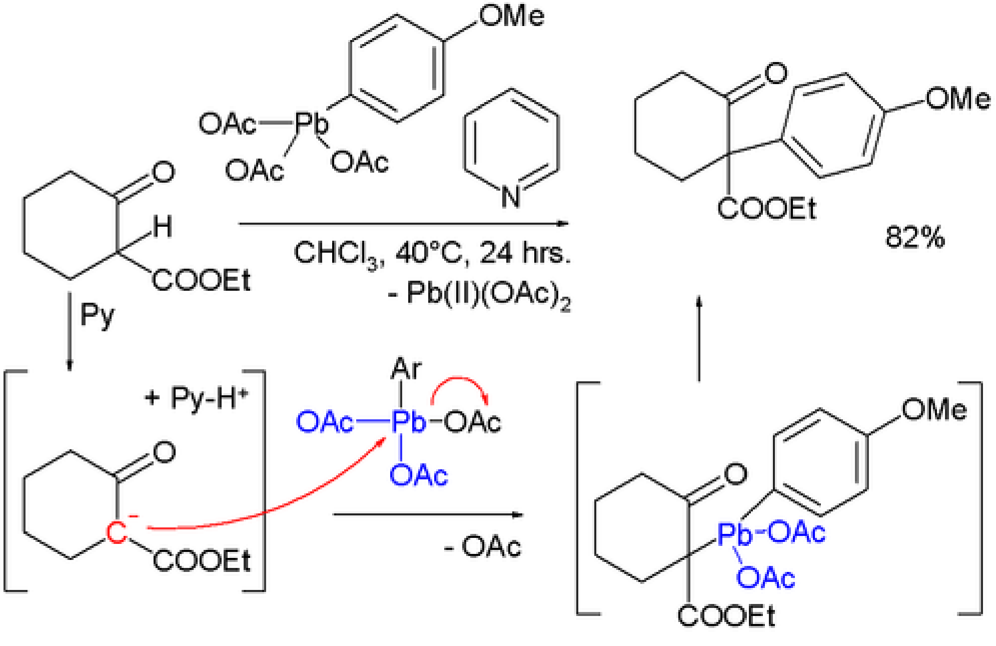
Aryllead triacetates

The lead substituent in *p*-methoxyphenyllead triacetate is displaced by carbon nucleophiles, such as the phenol mesitol, exclusively at the aromatic ortho position:[5]



The reaction requires the presence of a large excess of a coordinating amine such as pyridine which presumably binds to lead in the course of the reaction. The reaction is insensitive to radical scavengers and therefore a free radical mechanism can be ruled out. The reaction mechanism is likely to involve nucleophilic displacement of an acetate group by the phenolic group to a diorganolead intermediate which in some related reactions can be isolated. The second step is then akin to a Claisen rearrangement except that the reaction depends on the electrophilicity (hence the ortho preference) of the phenol.

The nucleophile can also be the carbanion of a β-dicarbonyl compound:



The carbanion forms by proton abstraction of the acidic α-proton by pyridine (now serving a double role) akin to the Knoevenagel condensation. This intermediate displaces an acetate ligand to a diorganolead compound and again these intermediates can be isolated with suitable reactants as unstable intermediates. The second step is reductive elimination with formation of a new C–C bond and lead(II) acetate.

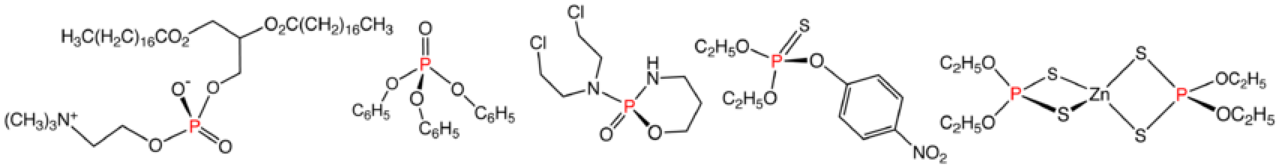
Organophosphorus compound

Organophosphorus compounds are organic compounds containing phosphorus. They are used primarily in pest control as an alternative to chlorinated hydrocarbons that persist in the environment. Some organophosphorus compounds are highly effective insecticides, although some are extremely toxic to humans, including sarin and VX nerve agents.

Organophosphorus(V) compounds, main categories

Phosphate esters and amides

Phosphate esters have the general structure $P(=O)(OR)_3$ feature P(V). Such species are of technological importance as flame retardant agents, and plasticizers. Lacking a P−C bond, these compounds are in the technical sense not organophosphorus compounds but esters of phosphoric acid. Many derivatives are found in nature, such as phosphatidylcholine. Phosphate ester are synthesized by alcoholysis of phosphorus oxychloride. A variety of mixed amido-alkoxo derivatives are known, one medically significant example being the anti-cancer drug cyclophosphamide. Also derivatives containing the thiophosphoryl group (P=S) include the pesticide malathion. The organophosphates prepared on the largest scale are the zinc dithiophosphates, as additives for motor oil. Several million kilograms of this coordination complex are produced annually by the reaction of phosphorus pentasulfide with alcohols.[6]



Illustrative organophosphates and related compounds: phosphatidylcholine, triphenylphosphate, cyclophosphamide, parathion, and zinc dithiophosphate.

Phosphine oxides, imides, and chalcogenides

Phosphine oxides (designation $\sigma^4\lambda^5$) have the general structure $R_3P=O$ with formal oxidation state V. Phosphine oxides form hydrogen bonds and some are therefore soluble in water. The P=O bond is very polar with a dipole moment of 4.51 D for triphenylphosphine oxide.

Compounds related to phosphine oxides include phosphine imides (R_3PNR') and related chalcogenides (R_3PE, where E = S, Se, Te). These compounds are some of the most thermally stable organophosphorus compounds.

Phosphonium salts and phosphoranes

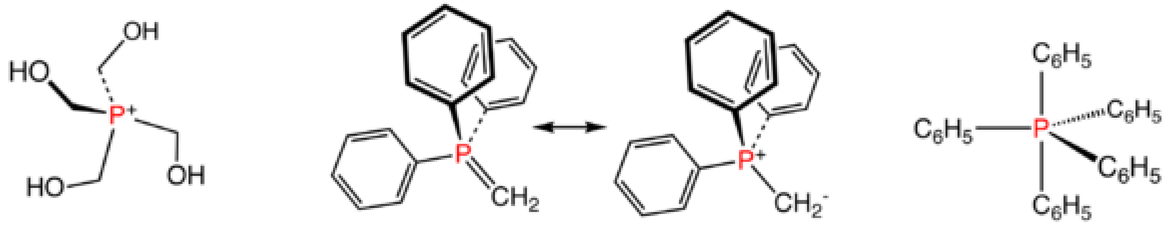
Compounds with the formula $[PR_4^+]X^-$ comprise the phosphonium salts. These species are tetrahedral phosphorus(V) compounds. From the commercial perspective, the most important member is tetrakis(hydroxymethyl)phosphonium chloride, $[P(CH_2OH)_4]Cl$, which is used as a fire retardant in textiles. Approximately 2M kg are produced annually of the chloride and the related sulfate.[6] They are generated by the reaction of phosphine with formaldehyde in the presence of the mineral acid:

$$PH_3 + HX + 4\ CH_2O \rightarrow [P(CH_2OH)_4^+]X^-$$

A variety of phosphonium salts can be prepared by alkylation and arylation of organophosphines:

$$PR_3 + R'X \rightarrow [PR_3R'^+]X^-$$

The methylation of triphenylphosphine is the first step in the preparation of the Wittig reagent.



Illustrative phosphorus(V) compounds: the phosphonium ion $P(CH_2OH)_4^+$, two resonance structures for the Wittig reagent Ph_3PCH_2, and pentaphenylphosphorane, a rare pentaorganophophorus compound.

The parent phosphorane ($\sigma^5\lambda^5$) is PH_5, which is unknown. Related compounds containing both halide and organic substituents on phosphorus are fairly common. Those with five organic substituents are rare, although $P(C_6H_5)_5$ is known, being derived from $P(C_6H_5)_4^+$ by reaction with phenyllithium.

Phosphorus ylides are unsaturated phosphoranes, known as Wittig reagents, e.g. $CH_2P(C_6H_5)_3$. These compounds feature tetrahedral phosphorus(V) and are considered relatives of phosphine oxides. They also are derived from phosphonium salts, but by deprotonation not alkylation.

Organophosphorus(III) compounds, main categories

Phosphites, phosphonites, and phosphinites

Phosphites, sometimes called phosphite esters, have the general structure $P(OR)_3$ with oxidation state +3. Such species arise from the alcoholysis of phosphorus trichloride:

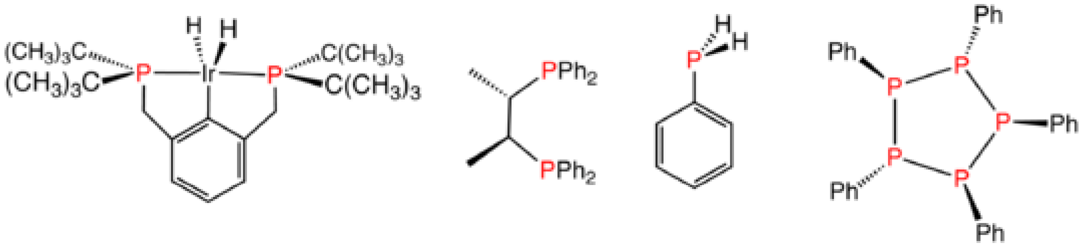
$$PCl_3 + 3\ ROH \rightarrow P(OR)_3 + 3\ HCl$$

The reaction is general, thus a vast number of such species are known. Phosphites are employed in the Perkow reaction and the Michaelis–Arbuzov reaction. They also serve as ligands in organometallic chemistry.

Intermediate between phosphites and phosphines are phosphonites ($P(OR)_2R'$) and phosphinite ($P(OR)R'_2$). Such species arise via alcoholysis reactions of the corresponding phosphinous and phosphonous chlorides (($PClR'_2$) and PCl_2R', respectively).

Phosphines

The parent compound of the phosphines is PH_3, called phosphine in the US and British Commonwealth, but phosphane elsewhere. Replacement of one or more hydrogen centers by an organic substituents (alkyl, aryl), gives $PH_{3-x}R_x$, an organophosphine, generally referred to as phosphines.



Various reduced organophosphorus compounds: a complex of an organophosphine pincer ligand, the chiral diphosphine used in homogeneous catalysis, the primary phosphine $PhPH_2$, and the phosphorus(I) compound $(PPh)_5$. Reactions

Organophosphines are nucleophiles and ligands. Two major applications are as reagents in the Wittig reaction and as supporting phosphine ligands in homogeneous catalysis.

Their nucleophilicity is evidenced by their reactions with alkyl halides to give phosphonium salts. Phosphines are nucleophilic catalysts in organic synthesis, e.g. the Rauhut–Currier reaction and Baylis-Hillman reaction.

Phosphines are reducing agents, as illustrated in the Staudinger reduction for the conversion of organic azides to amines and in the Mitsunobu reaction for converting alcohols into esters. In these processes, the phosphine is oxidized to phosphorus(V). Phosphines have also been found to reduce activated carbonyl groups, for instance the reduction of an α-keto ester to an α-hydroxy ester in *scheme 2*. In the proposed reaction mechanism, the first proton is on loan from the methyl group in trimethylphosphine (triphenylphosphine does not react).

Primary and secondary phosphines

In addition to the other reactions associated with phosphines, those bearing P-H groups exhibit additional reactivity associated with the P-H bonds. They are readily deprotonated using strong bases to give phosphide anions. Primary and secondary phosphines are generally prepared by reduction of related phosphorus halides or esters.

Phosphaalkenes and phosphaalkynes

Compounds with carbon phosphorus(III) multiple bonds are called phosphaalkenes ($R_2C{=}PR$) and phosphaalkynes ($RC{\equiv}P$). They are similar in structure, but not in reactivity, to imines ($R_2C{=}NR$) and nitriles ($RC{\equiv}N$), respectively. In the compound phosphorine, one carbon atom in benzene is replaced by phosphorus. Species of this type are relatively rare but for that reason are of interest to researchers. A general method for the synthesis of phosphaalkenes is by 1,2-elimination of suitable precursors, initiated thermally or by base such as DBU, DABCO, or triethylamine.

Organophosphorus(0), (I), and (II) compounds

Compounds where phosphorus exists in a formal oxidation state of less than III are uncommon, but examples are known for each class. Organophosphorus(0) species are debatably illustrated by the carbene adducts, $[P(NHC)]_2$, where NHC is an N-heterocyclic carbene. With the formulae $(RP)_n$ and $(R_2P)_2$, respectively, compounds of phosphorus(I) and (II) are generated by reduction of the related organophosphorus(III) chlorides:

$$5\ PhPCl_2 + 5\ Mg \rightarrow (PhP)_5 + 5\ MgCl_2$$

$$2\ Ph_2PCl + Mg \rightarrow Ph_2P\text{-}PPh_2 + MgCl_2$$

Diphosphenes, with the formula R_2P_2, formally contain phosphorus-phosphorus double bonds. These phosphorus(I) species are rare but are stable provided that the organic substituents are large enough to prevent catenation. Many mixed-valence compounds are known, e.g. the cage $P_7(CH_3)_3$.

Organoboron compound:

Organoborane or **organoboron** compounds are chemical compounds of boron and carbon that are organic derivatives of BH_3, for example trialkyl boranes. **Organoboron chemistry** or **organoborane chemistry** is the chemistry of these compounds. Organoboron compounds are important reagents in organic chemistry enabling many chemical transformations, the most important one called hydroboration.

preparation

From Grignard reagents

Simple organoboranes such as triethylborane or tris(pentafluorophenyl)boron can be prepared from trifluoroborane (as the ether complex) and the ethyl or pentafluorophenyl Grignard reagent. The borates (R_4B^- are generated via addition of R^--equivalents (RMgX, RLi, etc.) to R_3B).

From alkenes

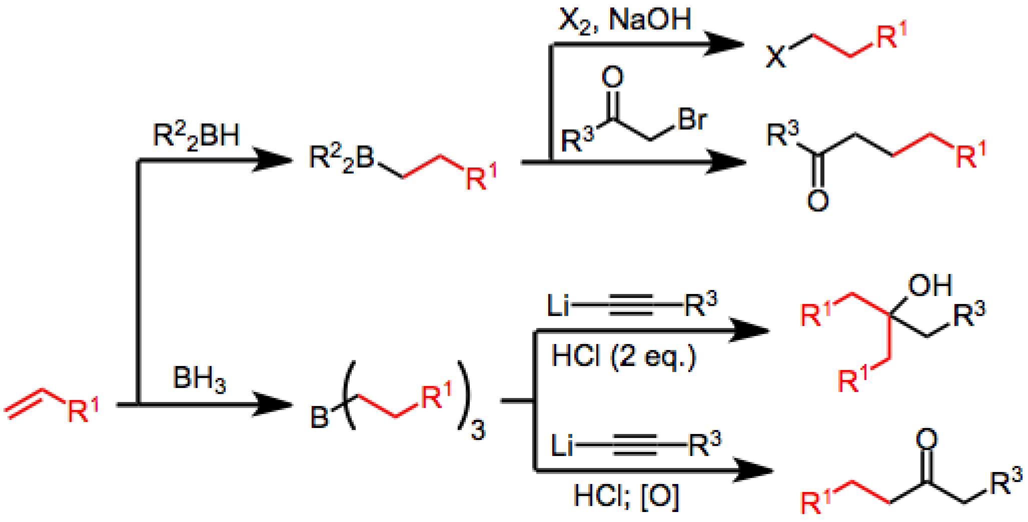
Alkenes insert into B-H bonds of boranes in a process called hydroboration. The process involves anti-Markovnikov addition. Hydroboration of alkenes or alkynes with borane (BH_3) or borane equivalents leads to the conversion of only 33% of the starting olefin to product after oxidation or protonolysis—the remaining olefin is incorporated into boron-containing byproducts. One organoboron reagent that is often employed in synthesis is 9-BBN. Hydroborations take place stereospecifically in a *syn* mode, that is on the same face of the alkene. In this concerted reaction the transition state is represented as a square with the corners occupied by carbon, carbon, hydrogen and boron with maximum overlap between the two olefin p-orbitals and the empty boron orbital.

By borylation

Metal-catalyzed C-H Borylation reactions are transition metal catalyzed organic reactions that produce an organoboron compound through functionalization of aliphatic and aromatic C-H bonds. A common reagent in this type of reaction is bis(pinacolato)diboron.

Reactions

Boron–carbon bonds are polarized toward carbon. Thus, the carbon attached to boron is nucleophilic. This property is harnessed to transfer one of the R groups to an electrophilic center either inter- or (more often) intramolecularly. In the latter case, the nucleophilic R group is able to undergo 1,2-migration towards an electrophilic carbon attached to boron. The resulting reorganized borane can then be oxidized or subjected to protonolysis to afford organic products:

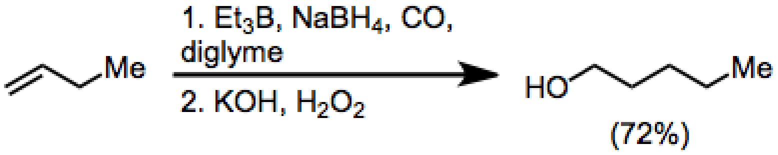


Hydroboration-oxidation

In organic synthesis the hydroboration reaction is taken further to generate other functional groups in the place of the boron group. The hydroboration-oxidation reaction offers a route to alcohols by oxidation of the borane with hydrogen peroxide or to the carbonyl group with the stronger oxidizing agent chromium oxide.

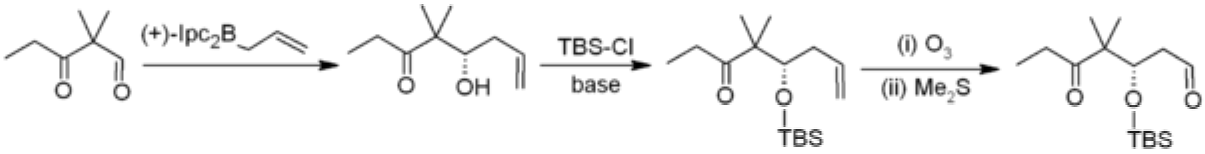
Rearrangements

Carbon monoxide is found to react with trialkylboranes. What follows is a 1,2-rearrangement whereby an alkyl substituent migrates from boron to the carbon of the carbonyl group. Homologated primary alcohols result from the treatment of organoboranes with carbon monoxide and a hydride.



Allylboration

Asymmetric allylboration demonstrates another useful application of organoboranes in carbon–carbon bond formation. In this example from Nicolaou's synthesis of the epothilones, asymmetric allylboration (using an allylborane derived from chiral alpha-pinene) is used in conjunction with TBS protection and ozonolysis. Overall, this provides a two-carbon homologation sequence that delivers the required acetogenin sequence.



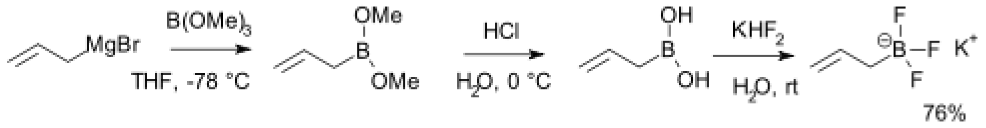
As reducing agent

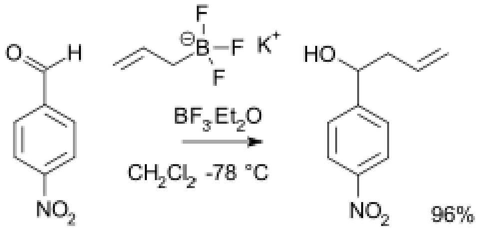
Borane hydrides such as 9-BBN and L-selectride (lithium tri-sec-butylborohydride) are reducing agents. An example of an asymmetric catalyst for carbonyl reductions is the CBS catalyst. This catalyst is also based on boron, the purpose of which is coordination to the carbonyl oxygen atom.

Borates

Trialkylboranes, BR_3, can be oxidized to the corresponding borates, $B(OR)_3$. One method for the determination of the amount of C-B bonds in a compound is by oxidation of R_3B with trimethylamine oxide (Me_3NO) to $B(OR)_3$. The trimethylamine (Me_3N) formed can then be titrated.

Boronic acids $RB(OH)_2$ react with potassium bifluoride $K[HF_2]$ to form trifluoroborate salts $K[RBF_3]$ which are precursors to nucleophilic alkyl and aryl boron difluorides, $ArBF_2$. The salts are more stable than the boronic acids themselves and used for instance in alkylation of certain aldehydes:



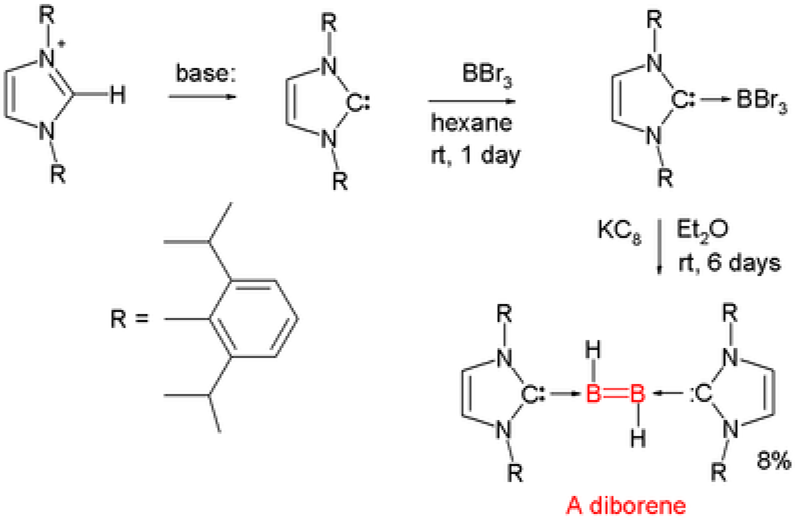


Suzuki reaction and related reactions

Organoboron compounds also lend themselves to transmetalation reactions, especially with organopalladium compounds. This reaction type is exemplified in the Suzuki reaction, which involves coupling of aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex.

Diborenes

Chemical compounds with boron to boron double bonds are rare.. Each boron atom has a proton attached to it and each boron atom is coordinated to a NHC carbene. The parent structure with the additional carbene ligands is diborane(2).



A reported diboryne is based on similar chemistry.

Uses:

TEB – Triethylborane was used to ignite the JP-7 fuel of the Pratt & Whitney J58 variable cycle engines powering the Lockheed SR-71 Blackbird.

UNIT III

CHEMISTRY OF ALCOHOLS, PHENOLS AND ETHERS

Nomenclature:

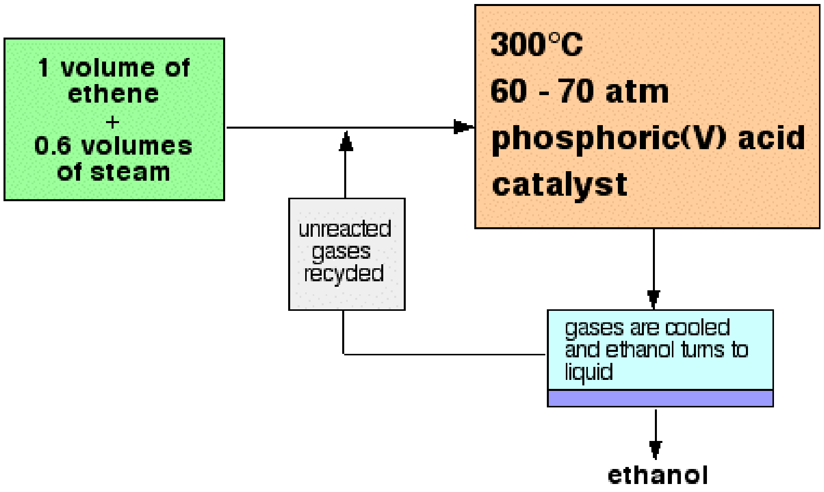
Alcohols are organic compounds in which a hydrogen atom of an aliphatic carbon is replaced with a hydroxyl group. Thus an alcohol molecule consists of two parts; one containing the alkyl group and the other containing functional group hydroxyl group.

Industrial Source of Alcohols:

Ethanol is manufactured by reacting ethene with steam. The catalyst used is solid silicon dioxide coated with phosphoric(V) acid. The reaction is reversible.

$$H_2C{=}CH_2(g) + H_2O(g) \xrightleftharpoons{H_3PO_4} CH_3CH_2OH(g)$$

Only 5% of the ethene is converted into ethanol at each pass through the reactor. By removing the ethanol from the equilibrium mixture and recycling the ethene, it is possible to achieve an overall 95% conversion. A flow scheme for the reaction looks like this:

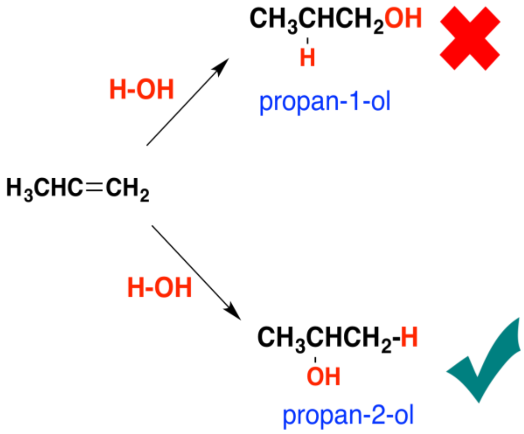


Preparation of Alcohols

Hydration of Alkenes:

The manufacture of other alcohols from alkenes

Some - but not all - other alcohols can be made by similar reactions. The catalyst used and the reaction conditions will vary from alcohol to alcohol. The reason that there is a problem with some alcohols is well illustrated with trying to make an alcohol from propene, $CH_3CH=CH_2$. In principle, there are two different alcohols which might be formed:



Oxymercuration:

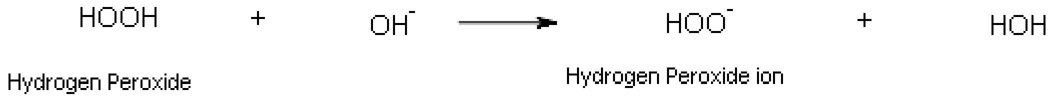
Carbocation rearrangement is a process in which the carbocation intermediate can form a more stable ion. With carbocation rearrangement, the reaction would not be able to hydrate quickly under mild conditions and be produced in high yields. This reaction is very fast and proceeds with 90% yield.

This reaction involves a mercury acting as a reagent attacking the alkene double bond to form a *Mercurinium Ion Bridge*. A water molecule will then attack the most substituted carbon to open the mercurium ion bridge, followed by proton transfer to solvent water molecule.

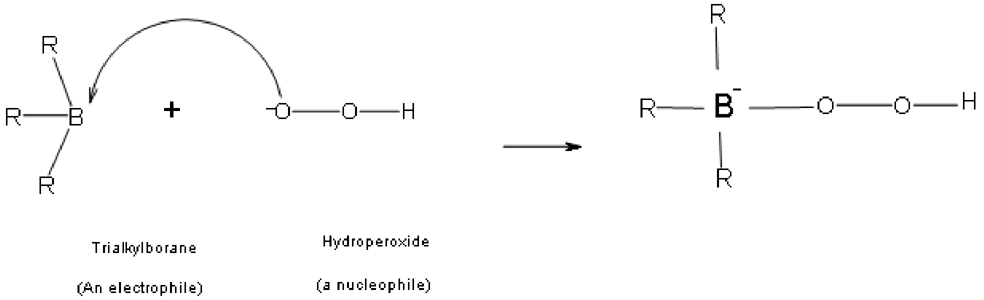
The organomercury intermediate is then reduced by sodium borohydride - the mechanism for this final step is beyond the scope of our discussion here. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's Regioselectivity with the OH group is attached to the most substituted carbon and the H is attach to the least substituted carbon. The reaction is useful, however, because strong acids are not required, and carbocation rearrangements are avoided because no discreet carbocation intermediate forms.

Hydroboration:

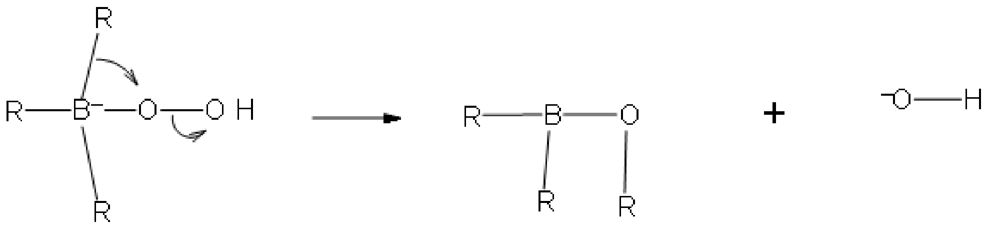
- Part 1: the first part of this mechanism deals with the donation of a pair of electrons from the hydrogen peroxide ion. the hydrogen peroxide is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from hydroboration.



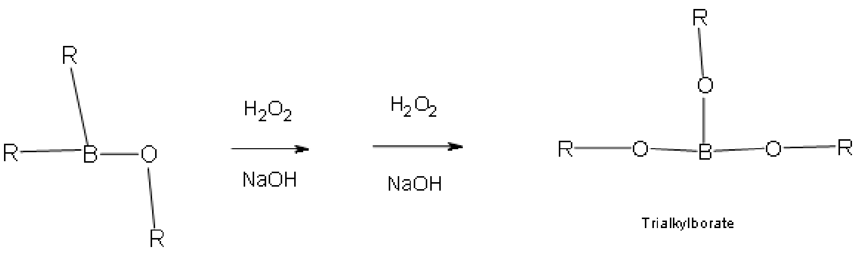
EpoxidationEpoxidation



- Part 2: In this second part of the mechanism, a rearrangement of an R group with its pair of bonding electrons to an adjacent oxygen results in the removal of a hydroxide ion.



Two more of these reactions with hydroperoxide will occur in order give a trialkylborate



- Part 3: This is the final part of the Oxidation process. In this part the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate.

$$\underset{\text{Trialkylborate}}{(RO)_3B} + 3\,NaOH \longrightarrow 3\,ROH + \underset{\text{Sodium Borate}}{Na_3BO_3}$$

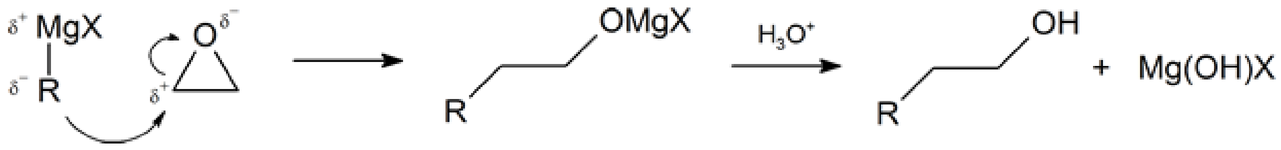
If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided here that will take you to other pages and media that are very helpful as well.

Grignard Addition:

Grignard reagents are among the most frequently used reagents in organic synthesis. They react with a wide variety of substrates; however, in this section, we are concerned only with those reactions that produce alcohols. Notice that in a reaction involving a Grignard reagent, not only does the functional group get changed, but the number of carbon atoms present also changes. This fact provides us with a useful method for ascending a homologous series. For example:

$$CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow[\text{ether}]{Mg} CH_3MgCl \xrightarrow[2.\ H_3O^+]{1.\ HCHO} CH_3CH_2OH$$

One important route for producing an alcohol from a Grignard reagent has been omitted from the discussion in the reading. It involves the reaction of the Grignard reagent with ethylene oxide to produce a primary alcohol containing two more carbon atoms than the original Grignard reagent.



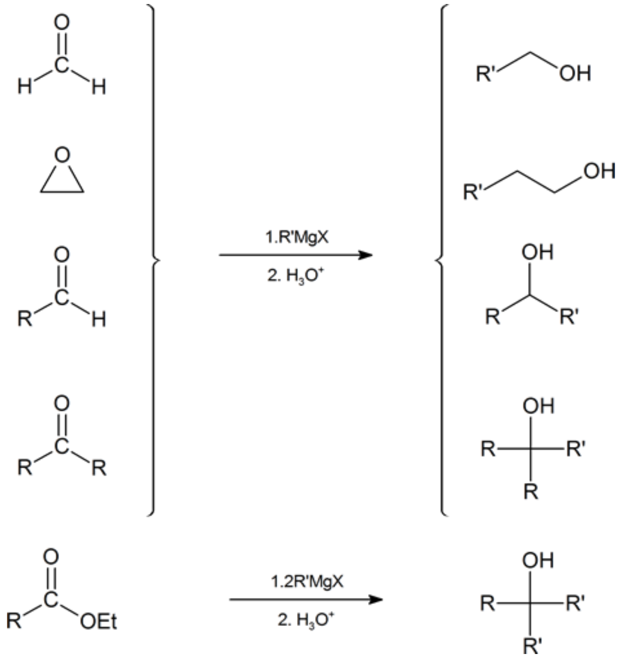
As mentioned in the reading, both organolithium and Grignard reagents are good nucleophiles.

They also act as strong bases in the presence of acidic protons such as $-CO_2H$, $-OH$, $-SH$, $-NH$ and terminal alkyne groups. Not only do acidic protons interfere with the nucleophilic attack on the carbonyl of these organometallic reagents, if the starting materials possess any acidic protons, reagents cannot be generated in the first place. They are also the reason these reactions must be carried out in a water-free environment.

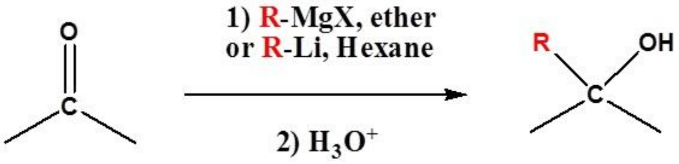
Another limitation of preparing Grignard and organolithium reagents is that they cannot already contain a carbonyl group (or other electrophilic multiple bonds like C=

N C≡N, N=O S=O) because it would simply react with itself.

A summary of the methods used to prepare alcohols from Grignard reagents is provided below.

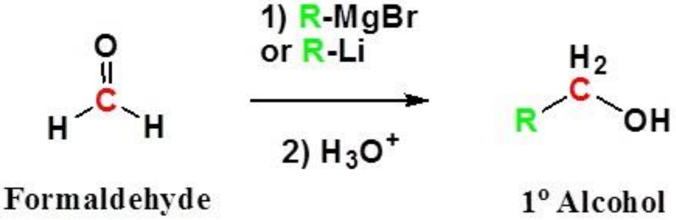


Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.

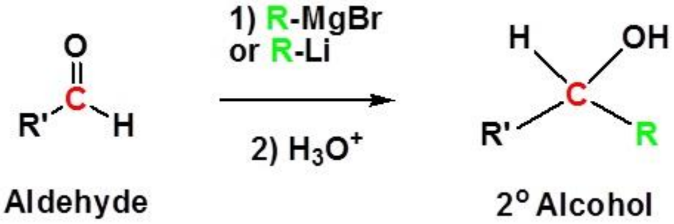


Both Grignard and Organolithium Reagents will perform these reactions

Addition to formaldehyde gives 1o alcohols



Addition to aldehydes gives 2^{o} alcohols



Addition to ketones gives 3o alcohols

Reduction:

The most common sources of the hydride Nucleophile are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminum is less electronegative than boron, the Al-H bond in $LiAlH_4$ is more polar, thereby, making $LiAlH_4$ a stronger reducing agent.

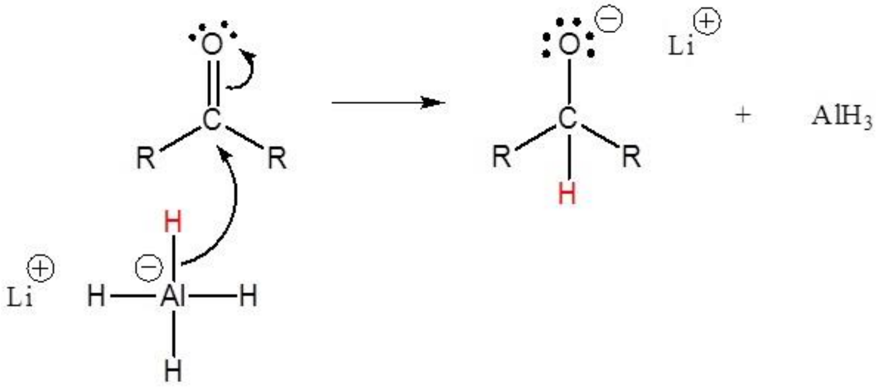
Addition of a hydride anion ($H:^-$) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1°-alcohols and ketones produce 2°-alcohols.

In metal hydrides reductions the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water is usually added in a second step. The lithium, sodium, boron and aluminum end up as soluble inorganic salts at the end of either reaction. Note! $LiAlH_4$ and $NaBH_4$ are both capable of reducing aldehydes and ketones to the corresponding alcohol.

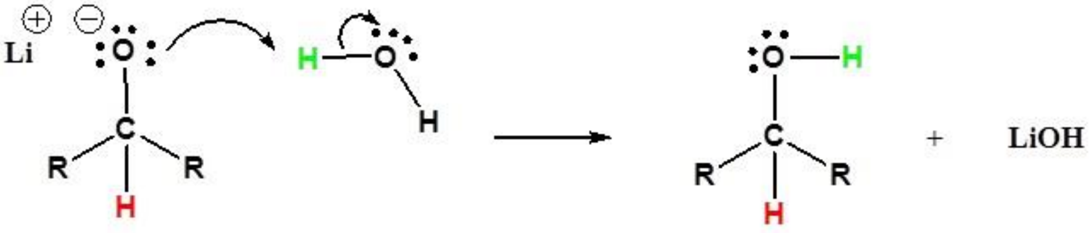
Mechanism

This mechanism is for a $LiAlH_4$ reduction. The mechanism for a $NaBH_4$ reduction is the same except methanol is the proton source used in the second step.

1) Nucleopilic attack by the hydride anion



2) The alkoxide is protonated



Physical Properties:

1. The Boiling Point of Alcohols

Alcohols generally have higher boiling points in comparison to other hydrocarbons having equal molecular masses. This is due to the presence of intermolecular hydrogen bonding between hydroxyl groups of alcohol molecules. In general, the boiling point of alcohols increases with an increase in the number of carbon atoms in the aliphatic carbon chain. On the other hand, the boiling point decreases with an increase in branching in aliphatic carbon chains the Van der Waals forces decreases with a decrease in surface area. Thus primary alcohols have a higher boiling point.

2. Solubility of Alcohols

The solubility of alcohol in water is governed by the hydroxyl group present. The hydroxyl group in alcohol is involved in the formation of intermolecular hydrogen bonding. Thus, hydrogen bonds are formed between water and alcohol molecules which make alcohol soluble in water. However, the alkyl group attached to the hydroxyl group is hydrophobic in nature. Thus, the solubility of alcohol decreases with the increase in the size of the alkyl group.

3. The Acidity of Alcohols

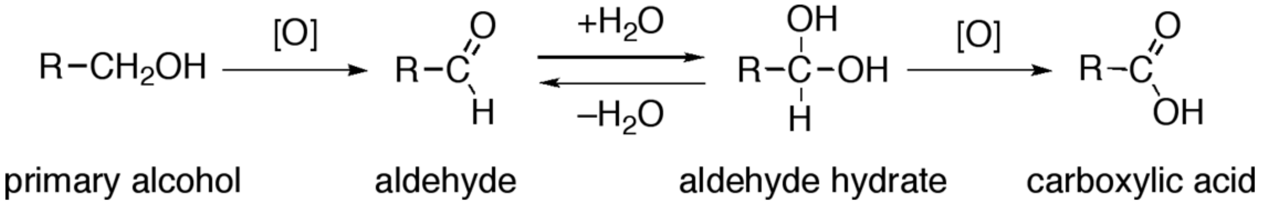
Alcohols react with active metals such as sodium, potassium etc. to form the corresponding alkoxide. These reactions of alcohols indicate their acidic nature. The acidic nature of alcohol is due to the polarity of –OH bond. The acidity of alcohols decreases when an electron-donating group is attached to the hydroxyl group as it increases the electron density on the oxygen atom. Thus, primary alcohols are generally more acidic than secondary and tertiary alcohols. Due to the presence of unshared electrons on the oxygen atom, alcohols act as Bronsted bases too.

Chemical Properties:

Alcohols exhibit a wide range of spontaneous chemical reactions due to the cleavage of the C-O bond and O-H bond. Some prominent chemical reactions of alcohols are:

1. Oxidation of Alcohol

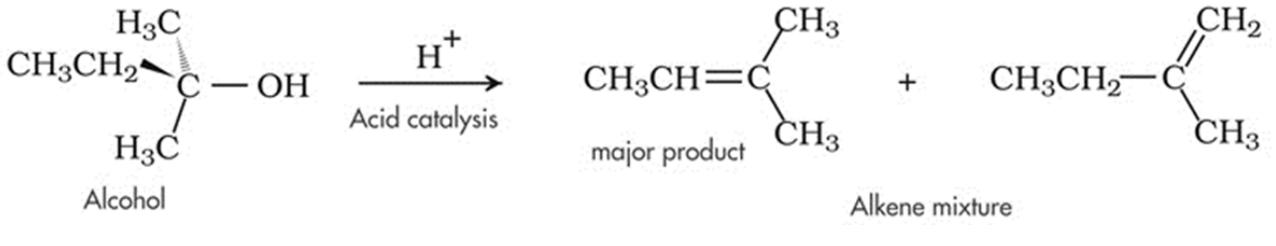
- Alcohols undergo oxidation in the presence of an oxidizing agent to produce aldehydes and ketones which upon further oxidation give carboxylic acids.



Alcohols: Physical and Chemical Properties

2. Dehydration of Alcohol

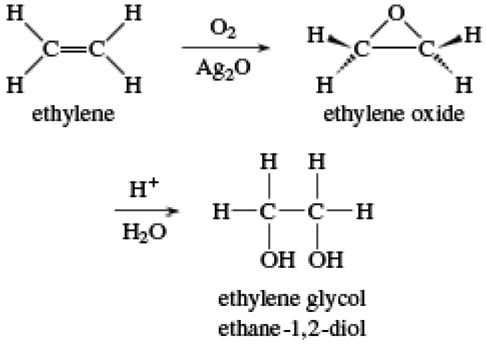
- Upon treatment with protic acids, alcohols undergo dehydration (removal of a molecule of water) to form alkenes. Dehydration of alcohol



Uses :

Glycols From Dihydroxylation:

glycol, also called **ethane-1,2-diol**, the simplest member of the glycol family of organic compounds. A glycol is an alcohol with two hydroxyl groups on adjacent carbon atoms (a 1,2-diol). The common name *ethylene glycol* literally means "the glycol derived from ethylene."



Ethylene glycol is a clear, sweet, slightly viscous liquid that boils at 198 °C (388.4 °F). Its most common use is as an automotive antifreeze. A 1:1 solution of ethylene glycol and water boils at 129 °C (264.2 °F) and freezes at −37 °C (−34.6 °F), serving as an excellent coolant in automotive radiators. Ethylene glycol is highly poisonous; animals or humans that drink the solution become very ill and may die.

Uses:

In addition to its use in antifreeze

Ethylene glycol is used as an ingredient in hydraulic fluids,

Printing inks, and paint solvents.

It is also used as a reagent in making polyesters

Explosives,

Alkyd resins

Synthetic waxes.

Glycerols:

Molecular formula $HOCH_2CHOHCH_2OH$.

Properties:

Its a a clear solution

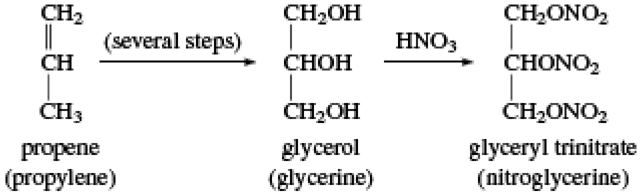
Colourless,

Viscous

Sweet-tasting liquid.

Uses:

Glycerol has numerous uses. It is a basic ingredient in the gums and resins used to make many modern protective coatings such as automotive enamels and exterior house paints. Glycerin reacted with nitric and sulfuric acid forms the explosive nitroglycerin (or nitroglycerine).



Glycerol is also a component of mono- and diglyceride emulsifiers, which are used as softening agents in baked goods, plasticizers in shortening, and stabilizers in ice cream. Its varied uses in the pharmaceutical and toilet goods fields include skin lotions, mouthwashes, cough medicines, drug solvents, serums, vaccines, and suppositories. Another significant use is as a protective medium for freezing red blood cells, sperm cells, eye corneas, and other living tissues. At one time, its largest single use was as automotive antifreeze; methanol and ethylene glycol have replaced it for this purpose.

Fats and oils are valued chiefly as sources of the carboxylic acids that are present, combined in the form of esters with glycerol. When the acids are set free from these compounds, glycerol remains as a solution in water and is purified by coagulating and settling extraneous matter, evaporating the water, and distilling.

Preparation of Phenols :

Phenol:

Phenol, any of a family of organic compounds characterized by a hydroxyl (—OH) group attached to a carbon atom that is part of an aromatic ring. Besides serving as the generic name for the entire family, the term *phenol* is also the specific name for its simplest member, monohydroxybenzene (C_6H_5OH), also known as benzenol, or carbolic acid.

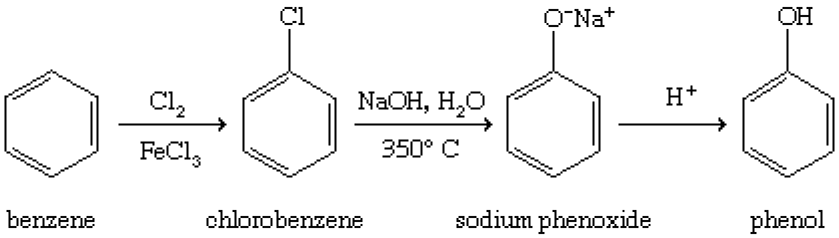
Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic.

Most of the phenol used today is produced from benzene, through either hydrolysis of chlorobenzene or oxidation of isopropylbenzene (cumene).

Synthesis:

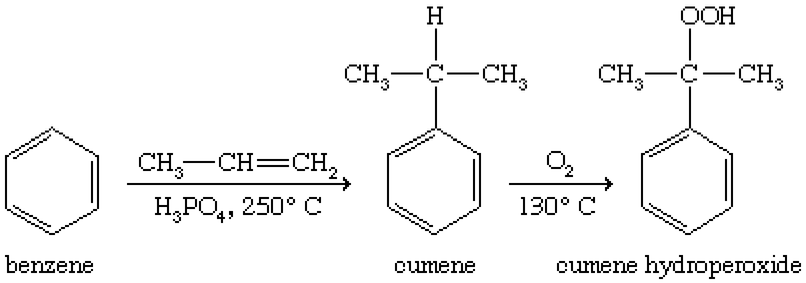
Hydrolysis of chlorobenzene (the Dow process)

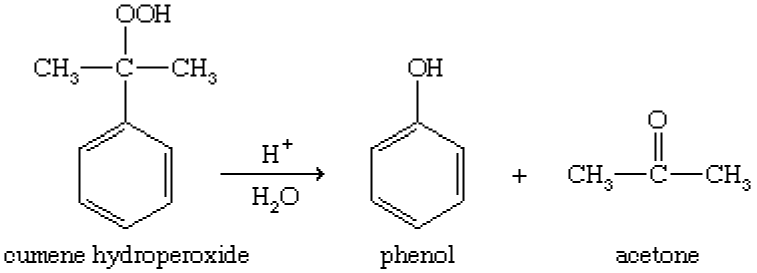
Benzene is easily converted to chlorobenzene by a variety of methods, one of which is the Dow process. Chlorobenzene is hydrolyzed by a strong base at high temperatures to give a phenoxide salt, which is acidified to phenol.



Oxidation of isopropylbenzene

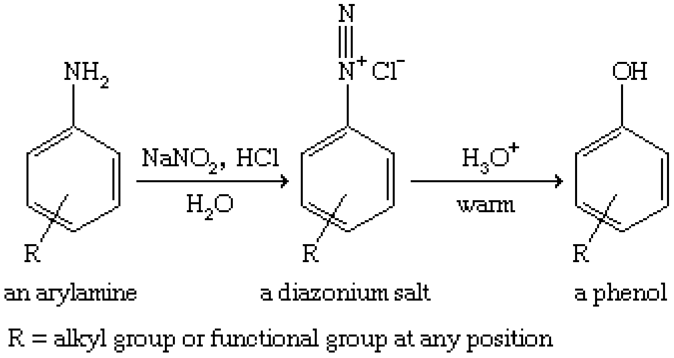
Benzene is converted to isopropylbenzene (cumene) by treatment with propylene and an acidic catalyst. Oxidation yields a hydroperoxide (cumene hydroperoxide), which undergoes acid-catalyzed rearrangement to phenol and acetone. Although this process seems more complicated than the Dow process, it is advantageous because it produces two valuable industrial products: phenol and acetone.





General synthesis of phenols

To make more-complicated phenolic compounds, a more general synthesis is needed. The cumene hydroperoxide reaction is fairly specific to phenol itself. The Dow process is somewhat more general, but the stringent conditions required often lead to low yields, and they may destroy any other functional groups on the molecule. A milder, more general reaction is the diazotization of an arylamine (a derivative of aniline, $C_6H_5NH_2$) to give a diazonium salt, which hydrolyzes to a phenol. Most functional groups can survive this technique, as long as they are stable in the presence of dilute acid.

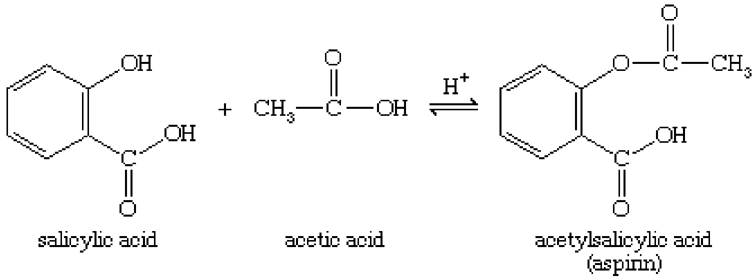


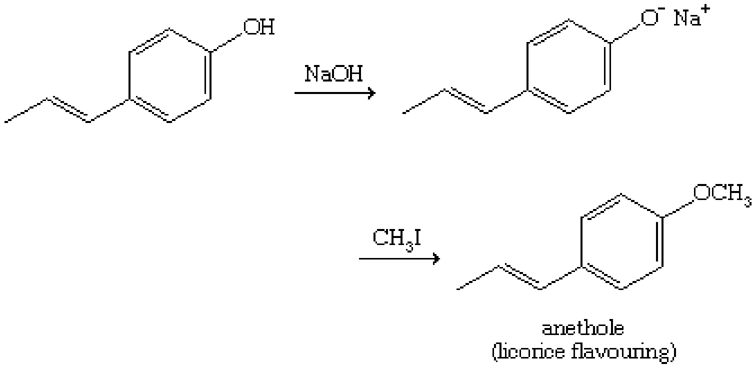
Physical properties:

Similar to alcohols, phenols have hydroxyl groups that can participate in intermolecular hydrogen bonding; in fact, phenols tend to form stronger hydrogen bonds than alcohols. (*See* chemical bonding: Intermolecular forces for more information about hydrogen bonding.) Hydrogen bonding results in higher melting points and much higher boiling points for phenols than for hydrocarbons with similar molecular weights. For example, phenol (molecular weight [MW] 94, boiling point [bp] 182 °C [359.6 °F]) has a boiling point more than 70 degrees higher than that of toluene ($C_6H_5CH_3$; MW 92, bp 111 °C [231.8 °F]).

Chemical Properties:

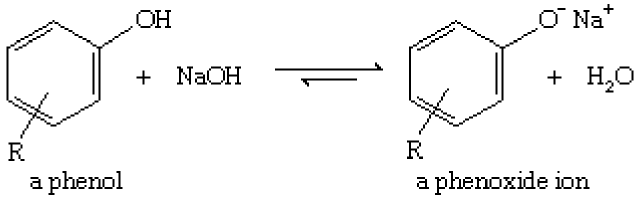
Much of the chemistry of phenols is like that of alcohols. For example, phenols react with acids to give esters, and phenoxide ions (ArO^-) can be good nucleophiles in Williamson ether synthesis.





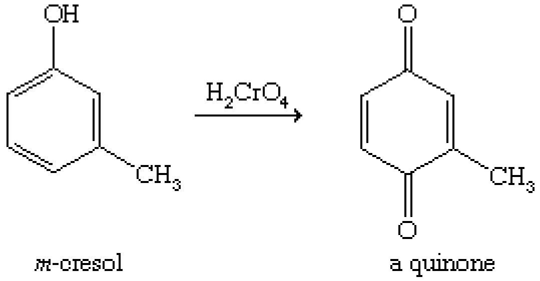
Acidity of phenols

Although phenols are often considered simply as aromatic alcohols, they do have somewhat different properties. The most obvious difference is the enhanced acidity of phenols. Phenols are not as acidic as carboxylic acids, but they are much more acidic than aliphatic alcohols, and they are more acidic than water. Unlike simple alcohols, most phenols are completely deprotonated by sodium hydroxide (NaOH).

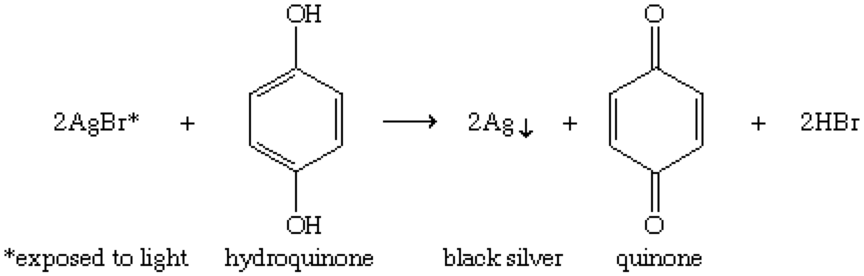


Oxidation

Like other alcohols, phenols undergo oxidation, but they give different types of products from those seen with aliphatic alcohols. For example, chromic acid oxidizes most phenols to conjugated 1,4-diketones called quinones. In the presence of oxygen in the air, many phenols slowly oxidize to give dark mixtures containing quinones.



Hydroquinone (1,4-benzenediol) is a particularly easy compound to oxidize, because it has two hydroxyl groups in the proper relationship to give up hydrogen atoms to form a quinone. Hydroquinone is used in developing photographic film by reducing activated (exposed to light) silver bromide (AgBr) to black metallic silver (Ag↓). Unexposed grains of silver bromide react more slowly than the exposed grains.



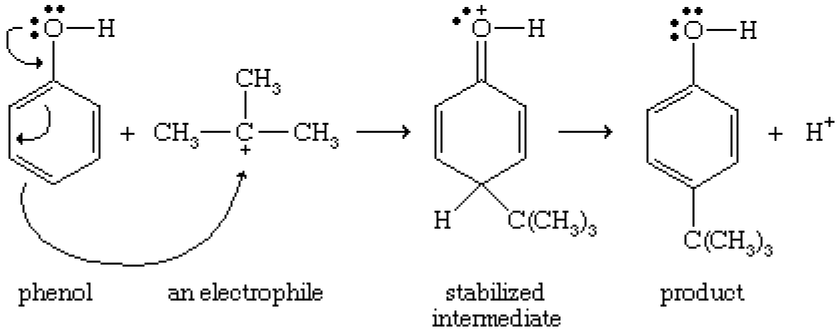
Uses:

Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic.

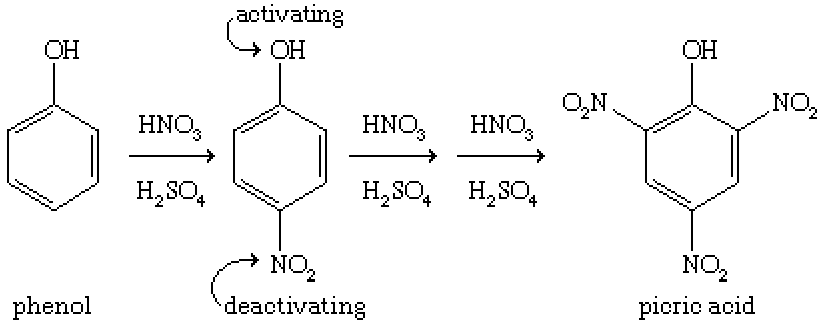
Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum

Aromatic Electrophilic Substitution Mechanism:

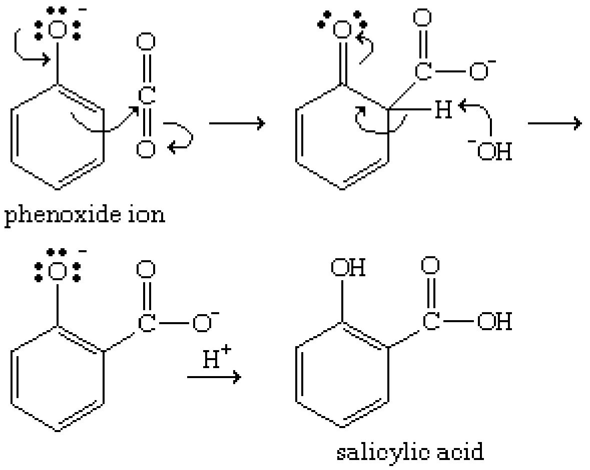
Phenols are highly reactive toward electrophilic aromatic substitution, because the nonbonding electrons on oxygen stabilize the intermediate cation. This stabilization is most effective for attack at the *ortho* or *para* position of the ring; therefore, the hydroxyl group of a phenol is considered to be activating (i.e., its presence causes the aromatic ring to be more reactive than benzene) and *ortho*- or *para*-directing.



Picric acid (2,4,6-trinitrophenol) is an important explosive that was used in World War I. An effective explosive needs a high proportion of oxidizing groups such as nitro groups. Nitro groups are strongly deactivating (i.e., make the aromatic ring less reactive), however, and it is often difficult to add a second or third nitro group to an aromatic compound. Three nitro groups are more easily substituted onto phenol, because the strong activation of the hydroxyl group helps to counteract the deactivation of the first and second nitro groups.



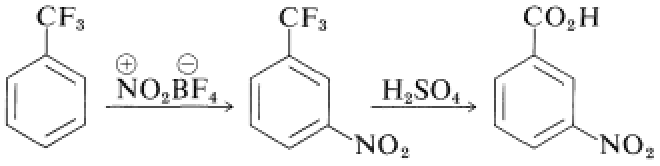
Phenoxide ions, generated by treating a phenol with sodium hydroxide, are so strongly activated that they undergo electrophilic aromatic substitution even with very weak electrophiles such as carbon dioxide (CO_2). This reaction is used commercially to make salicylic acid for conversion to aspirin and methyl salicylate.



Theory of Orientation And Reactivity:

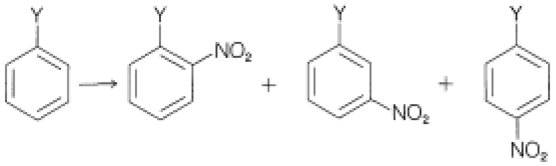
Basically, three experimental problems are involved in the substitution reactions of aromatic compounds: (1) proof of structure of the isomers that are formed; (2) determination of the percentage of each isomer formed, if the product is a mixture; and (3) measurement of the reactivity of the compound being substituted relative to some standard substance, usually benzene.

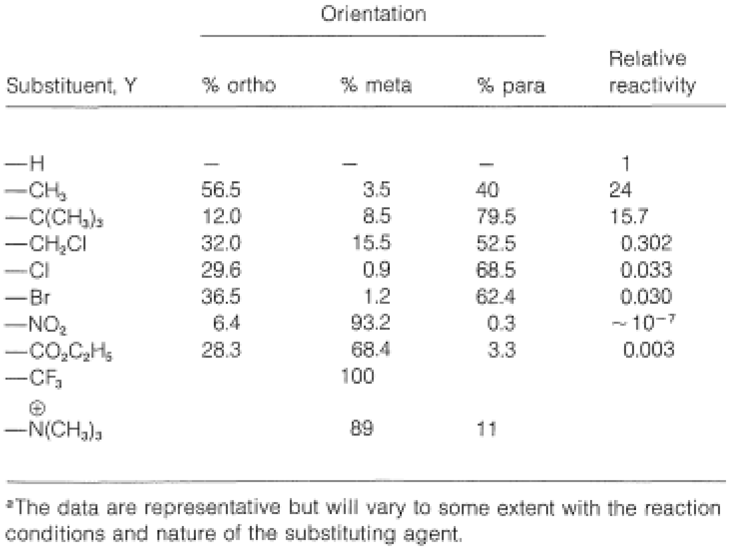
For benzenoid compounds, structures can be established by the historically important substitution method or with the aid of correlations between spectroscopic properties and positions of substitution. Also, it is often possible to identify the isomers by converting them to compounds of known structure. For example, trifluoromethylbenzene on nitration gives only one product, which has been shown to be the 3-nitro derivative by conversion to the known 3-nitrobenzoic acid by concentrated sulfuric acid:



The ratios of isomers formed in substitution reactions can be determined by spectroscopic means or by the analytical separation methods.

The reaction most studied in connection with the orientation problem is nitration, but the principles established also apply for the most part to the related reactions of halogenation, sulfonation, alkylation, and acylation. Some illustrative data for the nitration of a number of mono-substituted benzene derivatives are given in Table. The table includes the percentage of ortho, meta, and para isomers formed, along with their reactivities relative to benzene. We see that there is a wide range of reactivity according to the nature of the substituent, and that the ortho, meta, and para positions are *not* equally reactive. Although these substituent effects may appear complex.



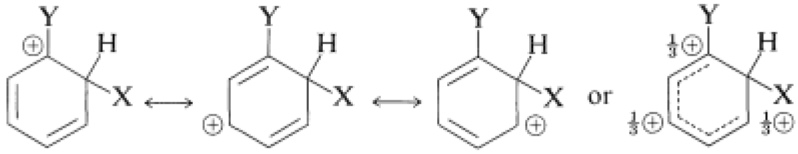


Substituent, Y	Orientation % ortho	 % meta	 % para	Relative reactivity
$—H$	–	–	–	1
$—CH_3$	56.5	3.5	40	24
$—C(CH_3)_3$	12.0	8.5	79.5	15.7
$—CH_2Cl$	32.0	15.5	52.5	0.302
$—Cl$	29.6	0.9	68.5	0.033
$—Br$	36.5	1.2	62.4	0.030
$—NO_2$	6.4	93.2	0.3	$\sim 10^{-7}$
$—CO_2C_2H_5$	28.3	68.4	3.3	0.003
$—CF_3$		100		
$—\overset{\oplus}{N}(CH_3)_3$		89	11	

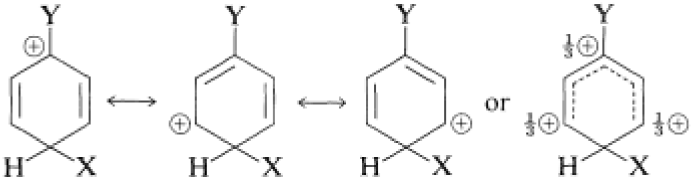
[a]The data are representative but will vary to some extent with the reaction conditions and nature of the substituting agent.

The positive charge in the ring is dispersed mainly on alternate carbons, as shown below.

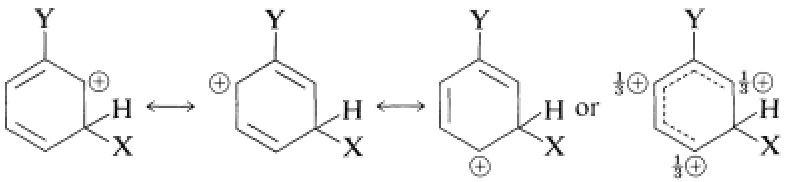
ortho substitution



para substitution

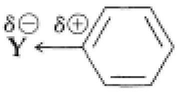


meta substitution



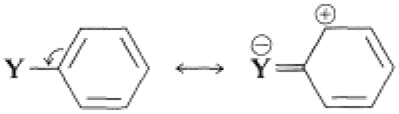
The substituent Y

should (and does) exert its electronic influence more strongly from the ortho and para positions than from the meta position because Y in the ortho and the para positions is close to a positively charged ring carbon. This electronic influence will be stabilizing if Y has a net electron-donating effect, and destabilizing if Y is electron withdrawing. A group can withdraw electrons relative to hydrogen if it is more electronegative than hydrogen and this is called the electron-withdrawing inductive effect. A group also can withdraw electrons by the **resonance effect**:



electron-withdrawing inductive effect

$Y = —CF_3, —\overset{\oplus}{N}R_3$



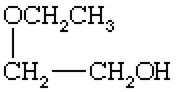
electron-withdrawing resonance effect

$Y = —NO_2, —CO_2R$

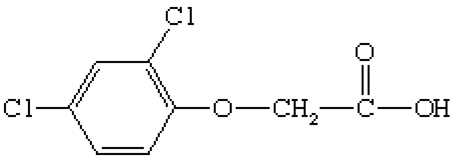
Ether compounds:

Common names of ethers simply give the names of the two alkyl groups bonded to oxygen and add the word *ether*. The current practice is to list the alkyl groups in alphabetical order (*t*-butyl methyl ether), but older names often list the alkyl groups in increasing order of size (methyl *t*-butyl ether). If just one alkyl group is described in the name, it implies two identical groups, as in ethyl ether for diethyl ether.

Systematic (IUPAC) names for ethers use the more complex group as the root name, with the oxygen atom and the smaller group named as an alkoxy substituent. Examples given above are ethoxyethane (diethyl ether), methoxyethane (methyl ethyl ether), 2-methoxy-2-methylpropane (MTBE), and phenoxybenzene (diphenyl ether). The IUPAC nomenclature works well for compounds with additional functional groups, because the other functional groups can be described in the root name.



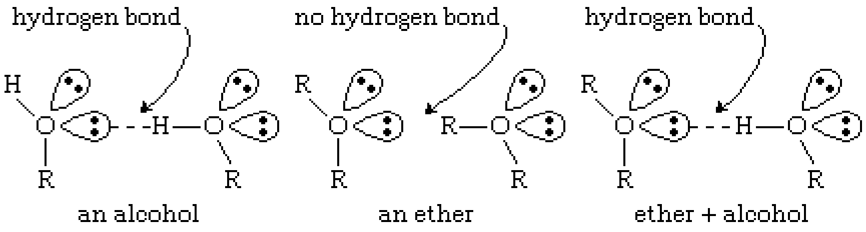
2-ethoxyethanol
(ethyl cellosolve)



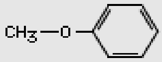
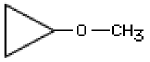
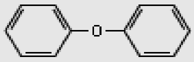
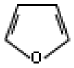
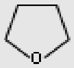
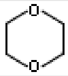
2,4-dichlorophenoxyacetic acid
(2,4-D herbicide)

Preparation of Ethers:

Ethers lack the hydroxyl groups of alcohols. Without the strongly polarized O—H bond, ether molecules cannot engage in hydrogen bonding with each other. Ethers do have nonbonding electron pairs on their oxygen atoms, however, and they can form hydrogen bonds with other molecules (alcohols, amines, etc.) that have O—H or N—H bonds. The ability to form hydrogen bonds with other compounds makes ethers particularly good solvents for a wide variety of organic compounds and a surprisingly large number of inorganic compounds. (For more information about hydrogen bonding, *see* chemical bonding: Intermolecular forces.)



Physical properties of ethers

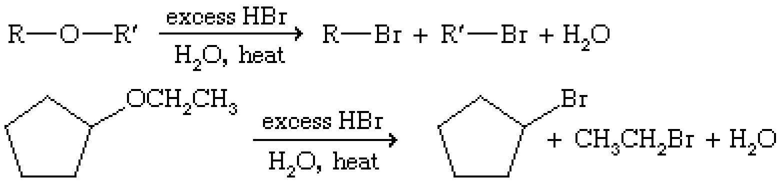
name	structure	mp (°C)	bp (°C)	density (grams per millilitre)
dimethyl ether	$CH_3—O—CH_3$	-140	-25	0.66
ethyl methyl ether	$CH_3CH_2—O—CH_3$		8	0.72
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	-116	35	0.71
dipropyl ether	$CH_3CH_2CH_2—O—CH_2CH_2CH_3$	-122	91	0.74
diisopropyl ether	$(CH_3)_2CH—O—CH(CH_3)_2$	-86	68	0.74
divinyl ether	$CH_2{=}CH—O—CH{=}CH_2$	-101	28	0.77
1,2-dimethoxyethane (DME)	$CH_3OCH_2CH_2OCH_3$	-58	83	0.86
methyl phenyl ether (anisole)		-37	154	0.99
cyclopropyl methyl ether		-119	45	0.81
diphenyl ether		27	259	1.07
furan		-86	32	0.94
tetrahydrofuran (THF)		-108	65	0.89
1,4-dioxane		11	101	1.03

Because ether molecules cannot engage in hydrogen bonding with each other, they have much lower boiling points than do alcohols with similar molecular weights. For example, the boiling point of diethyl ether ($C_4H_{10}O$, molecular weight [MW] 74) is 35 °C (95 °F), but the boiling point of 1-butanol (or *n*-butyl alcohol; $C_4H_{10}O$, MW 74) is 118 °C (244 °F). In fact, the boiling points of ethers are much closer to those of alkanes with similar molecular weights; the boiling point of pentane (C_5H_{12}, MW 72) is 36 °C (97 °F), close to the boiling point of diethyl ether.

Reactions of ethers

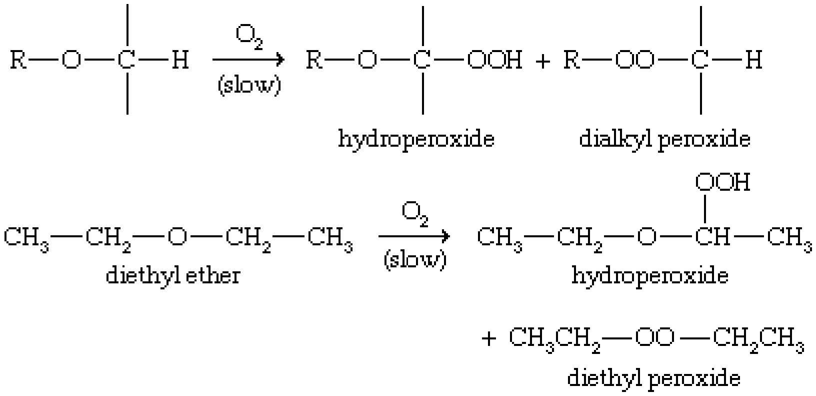
Cleavage

Ethers are good solvents partly because they are not very reactive. Most ethers can be cleaved, however, by hydrobromic acid (HBr) to give alkyl bromides or by hydroiodic acid (HI) to give alkyl iodides.



Autoxidation

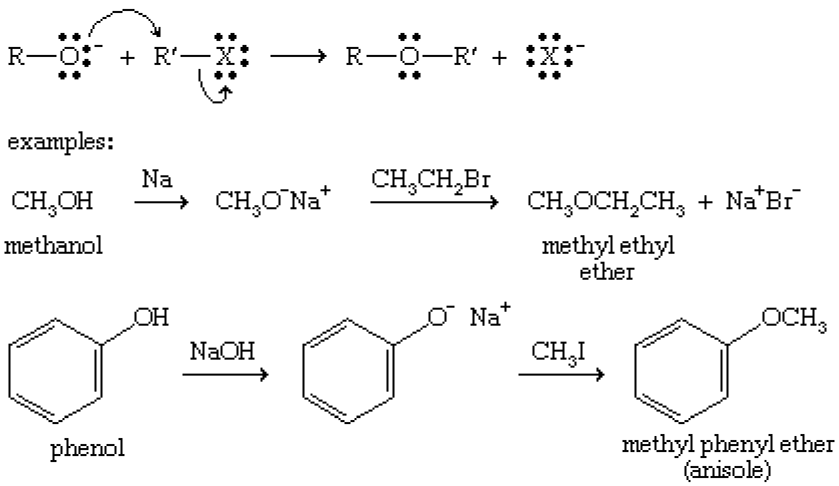
Autoxidation is the spontaneous oxidation of a compound in air. In the presence of oxygen, ethers slowly autoxidize to form hydroperoxides and dialkyl peroxides. If concentrated or heated, these peroxides may explode. To prevent such explosions, ethers should be obtained in small quantities, kept in tightly sealed containers, and used promptly.



Dehydration of Alcohols

Williamson's Synthesis:

The most versatile method for making ethers is the Williamson ether synthesis, named for English chemist Alexander Williamson, who devised the method in the 19th century. It uses an alkoxide ion to attack an alkyl halide, substituting the alkoxy (—O—R) group for the halide. The alkyl halide must be unhindered (usually primary), or elimination will compete with the desired substitution.

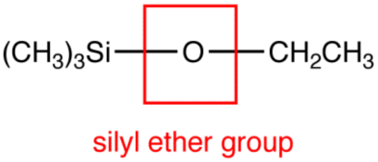


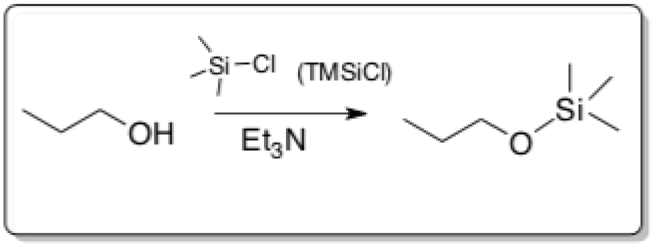
Silyl Ether:

- A silyl ether is the compound obtained when one or both carbon atoms bonded to the ether group in an ether molecule is replaced by silicon atoms.

  eg:

  - $(CH_3)_3Si—O—CH_2CH_3$
- The oxygen atom in a silyl ether molecule is called the silyl ether group.





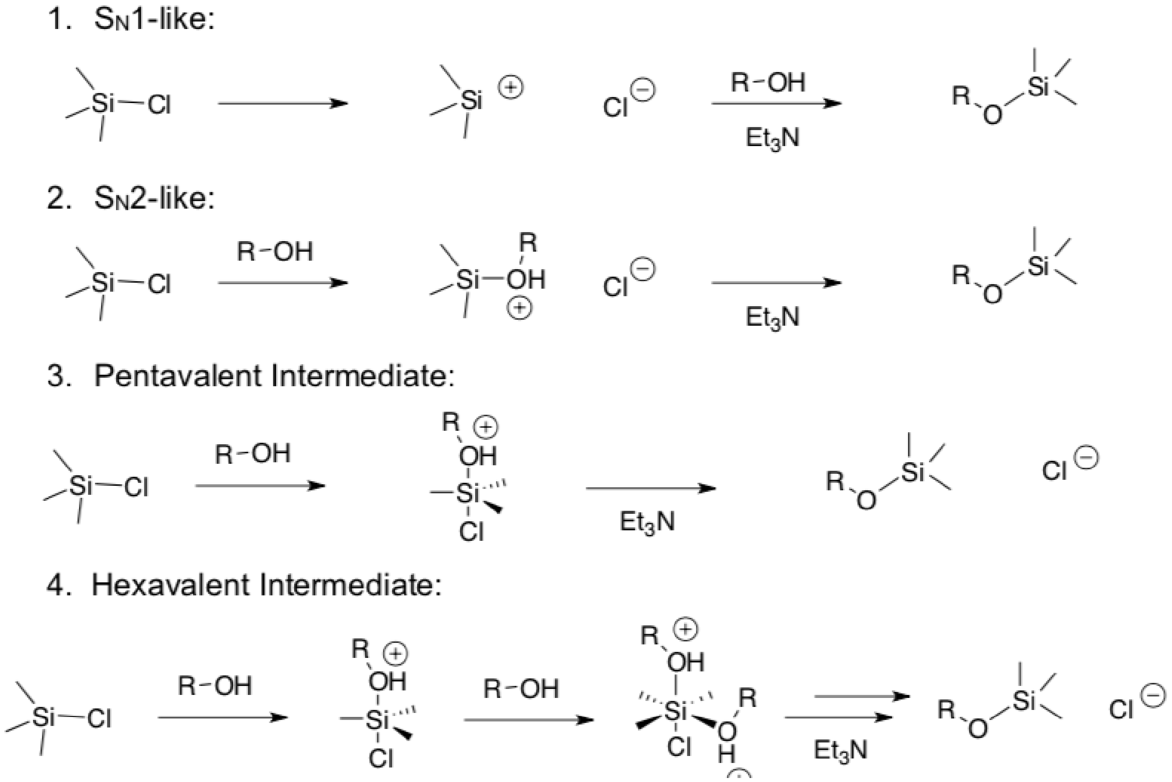
Formation of Silyl Ethers

Silyl ethers are functional groups with Si covalently bonded to an alkoxy group. Silyl ethers are inert to many reagents that react with alcohols, so they serve as protecting groups in organic synthesis.

Silicon is capable of making pentavalent and hexavalent complexes.

- Propose a reason. There are several hotly contested theories so there is no “right” answer.

Because of the ability to make 5 or 6 bonds, the mechanism for the formation of silyl ethers could proceed in four ways:

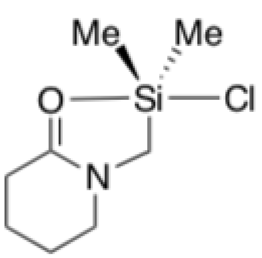


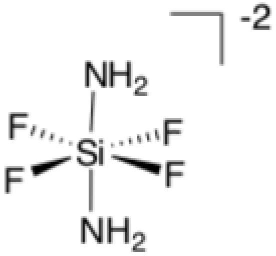
For each *of the mechanisms proposed above,*

- Draw the arrows showing electron flow.
- Circle the rds.
- Determine the molecularity of the reaction.

Mechanistic Studies

A number of complexes of the following type have been isolated and characterized by x-ray crystallography.





These complexes lend support to the existence of silicon complexes making 5 and 6 bonds.

- Which mechanisms have five and six coordinate reactive intermediates. The ability to make these stable structures supports the possibility of which reaction mechanisms? (circle one or two)

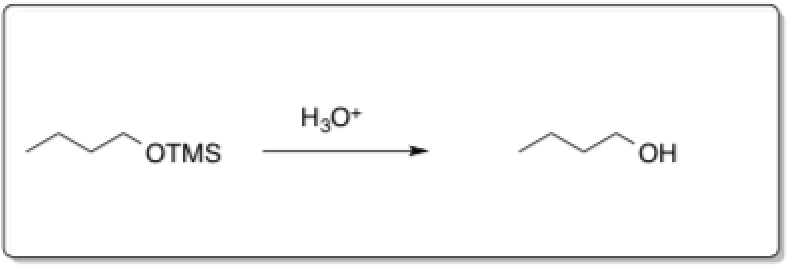
  SN1-like SN2-like Pentavalent Intermediate Hexavalent Intermediate

The kinetic data suggests that the reaction is **second order** in the nucleophilic alcohol.

- Which reaction mechanism does this data support? (circle one)

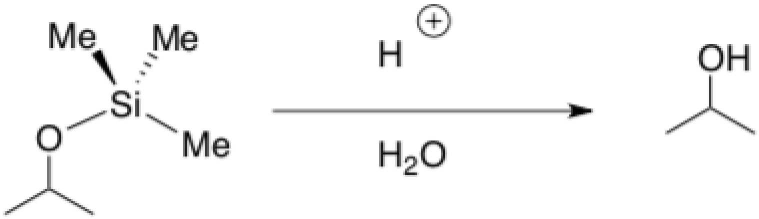
  SN1-like SN2-like Pentavalent Intermediate Hexavalent Intermediate

Removal of a Silyl Ether

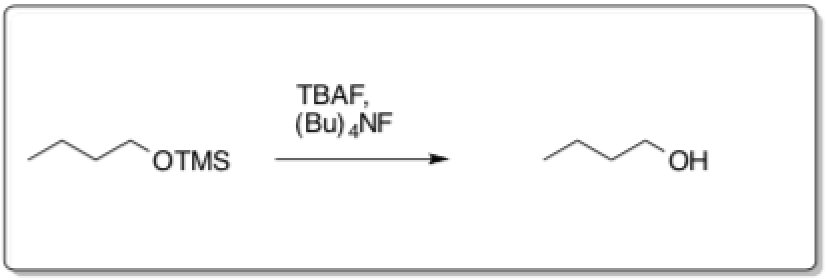


The silyl reaction is reversible. Often under acidic aqueous conditions.

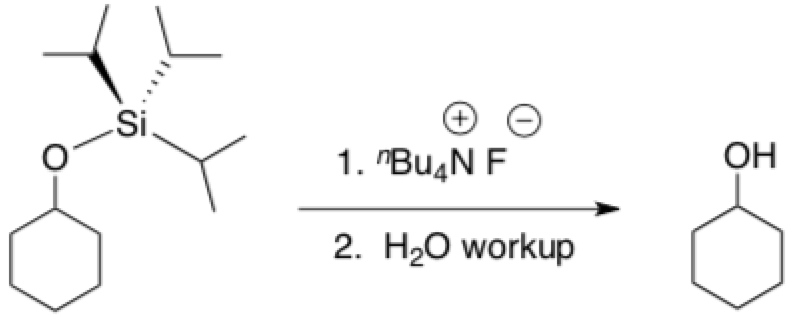
- Provide a likely mechanism with a hexavalent intermediate.



Bulkier silyl ethers are frequently cleaved via addition of fluoride salts using a similar mechanism. (Bu4NF is frequently abbreviated TBAF)



- Provide a likely mechanism for the reaction below. Include a hexavalent intermediate.



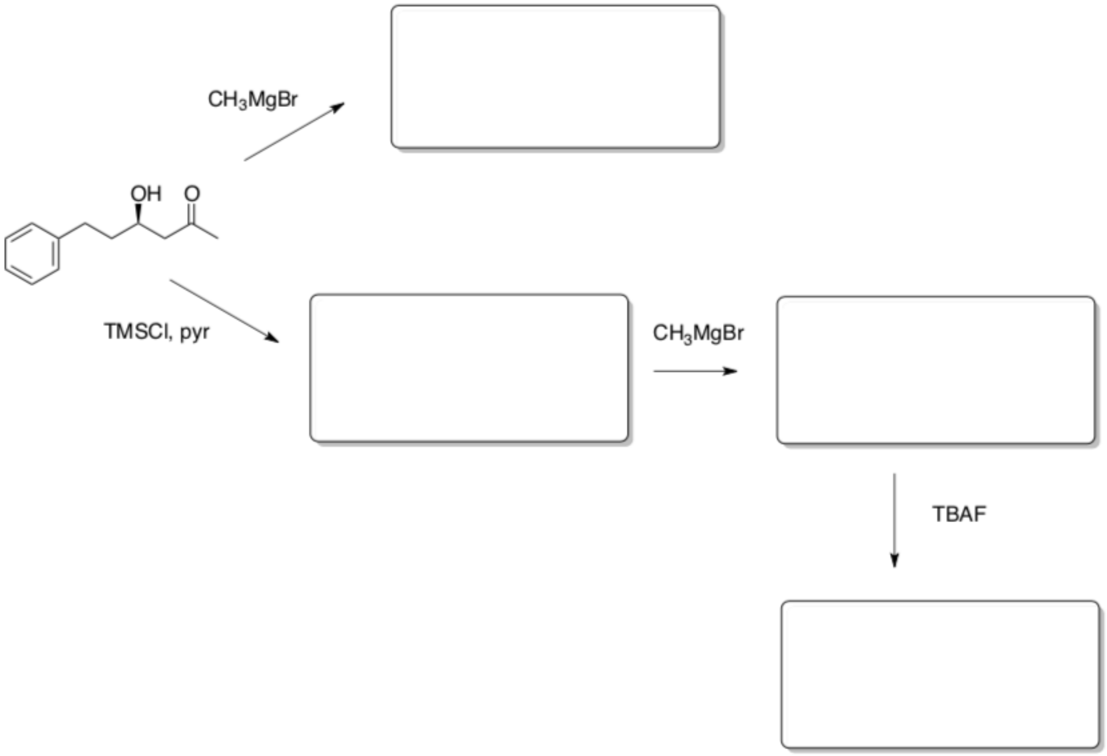
- Explain why this bulky silyl group can be reversed under with fluoride but not H_3O^+. Consider size of H_2O vs F^- as well as bond strengths (Si-O 108 kcal/mol; Si-F 135 kcal/mol).

Use of Silyl Ethers as Protecting Groups

Typically, silyl groups are added to alcohols when they might react with the reagent instead of the intended reaction.

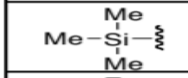
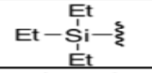
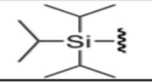
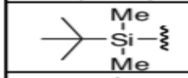
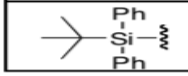
For example, Grignard reagents are strong bases and they tend to deprotonate alcohols rather than react with the carbonyl functional groups in the molecule.

- Complete the diagram below that shows this problem and how silyl groups can protect the alcohol functionality.



Common Silyl Ethers

Common silyl ethers are: trimethylsilyl (**TMS**), *tert*-butyldiphenylsilyl (**TBDPS**), *tert*-butyldimethylsilyl (**TBS/TBDMS**) and triisopropylsilyl (**TIPS**). They are particularly useful because they can be installed and removed very selectively under mild conditions.

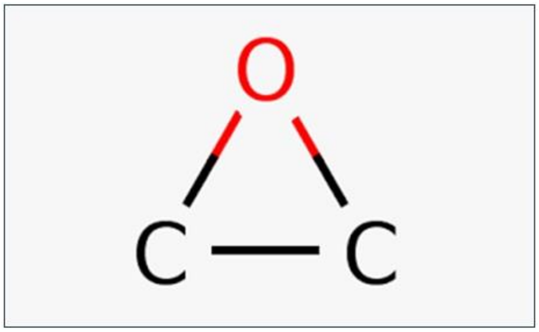
Structure	Name	Abbreviation
	trimethylsilyl	TMS
	triethylsilyl	TES
	triisopropylsilyl	TIPS
	*tert*-butyldimethyl	TBS
	di-*tert*-butylmethyl	DTBMS
	*tert*-butyldiphenyl	TBDPS

Small silyl ethers can be removed under acidic conditions.

Bulky ethers must be removed using TBAF (tetra-butyl ammonium fluoride).

Epoxide:

An epoxide is a cyclic ether which contains a three atom ring that approximates an equilateral triangle. These are highly reactive when compared to other ethers. The fundamental structure of it contains two carbon atoms of a hydrocarbon attached to an oxygen atom. The structure can be chemically shown as



Epoxide structure

Economically Ethylene oxide is the most important epoxide and is created by oxidation of ethylene over a silver catalyst. It is used as a fumigant and to make ethylene glycol, antifreeze and other useful compounds.

Epoxide synthesis:

Epoxide can be synthesized in many ways. Propylene oxide and Ethylene oxide are the two epoxides that are produced in a large scale, approximately 3 and 15 tonnes/year respectively.

- **Heterogeneously Catalyzed oxidation of alkenes**

When ethylene reacts with oxygen under a silver catalyst, epoxide is formed. According to stoichiometry, it can be chemically expressed as

$$7\ H_2C{=}CH_2 + 6\ O_2 \rightarrow 6\ C_2H_4O + 2\ CO_2 + 2\ H_2O$$

- **Homogeneously catalysed asymmetric epoxidation**

Chiral epoxides can be made from prochiral alkenes. Lot of metal complexes act as active catalysts and the most important among them are vanadium, molybdenum and titanium.

- **Nucleophilic epoxidation**

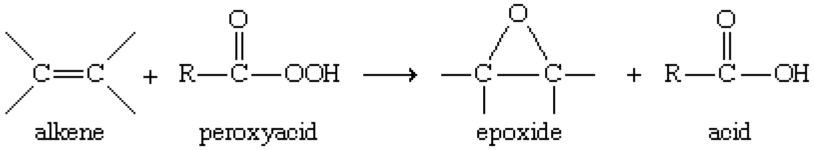
Electron deficient olefins can be epoxidized using compounds such as peroxides. This reaction has two steps: firstly, nucleophilic conjugate is added to an oxygen atom to give a stabilized carbanion.

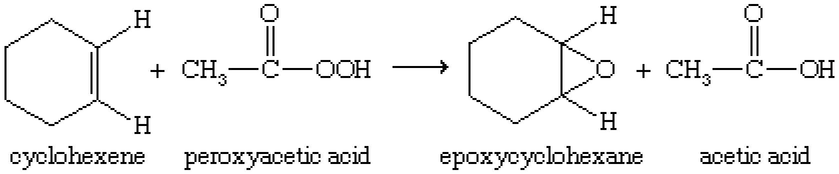
- **Biosynthesis**

Epoxides are not common in nature. They are produced generally by oxygenation of alkenes

Epoxides From Peracids:

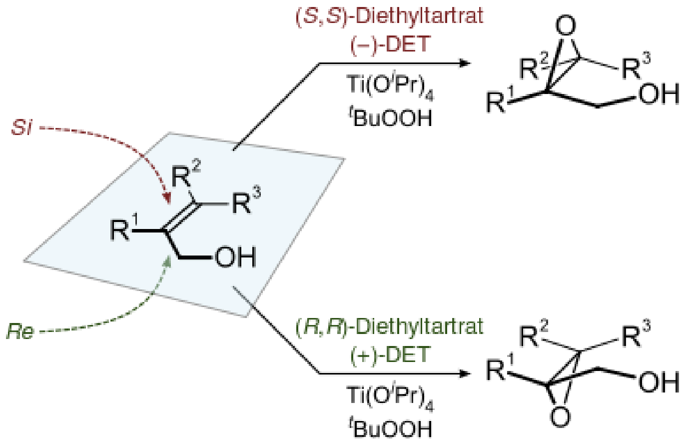
More-complex epoxides are commonly made by the epoxidation of alkenes, often using a peroxyacid (RCO_3H) to transfer an oxygen atom.





Sharpless Asymmetric Epoxidation:

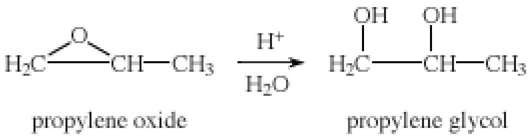
The **Sharpless epoxidation** reaction is an enantioselective chemical reaction to prepare 2,3-epoxyalcohols from primary and secondary allylic alcohols.



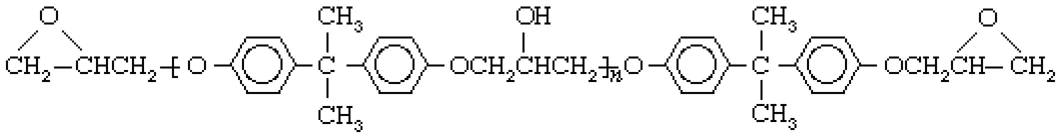
The stereochemistry of the resulting epoxide is determined by the enantiomer of the chiral tartrate diester (usually diethyl tartrate or diisopropyl tartrate) employed in the reaction. The oxidizing agent is *tert*-butyl hydroperoxide. Enantioselectivity is achieved by a catalyst formed from titanium tetra(isopropoxide) and diethyl tartrate. Only 5–10 mol% of the catalyst in the presence of 3Å molecular sieves (3Å MS) is necessary.

Reactions of Epoxides:

Epoxides are easily opened, under acidic or basic conditions, to give a variety of products with useful functional groups. For example, the acid- or base-catalyzed hydrolysis of propylene oxide gives propylene glycol.

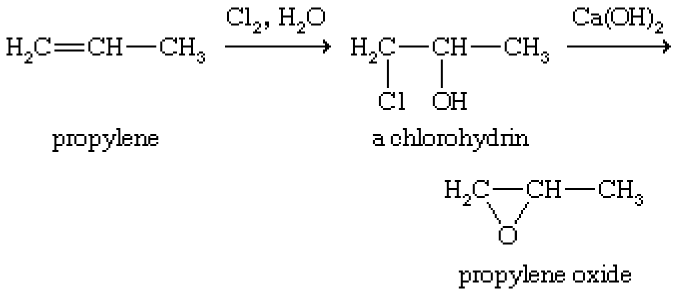


Epoxides can be used to assemble polymers known as epoxies, which are excellent adhesives and useful surface coatings. The most common epoxy resin is formed from the reaction of epichlorohydrin with bisphenol A.



Uses:

Another important industrial route to epoxides requires a two-step process. First, an alkene is converted to a chlorohydrin, and second, the chlorohydrin is treated with a base to eliminate hydrochloric acid, giving the epoxide; this is the method used to make propylene oxide.



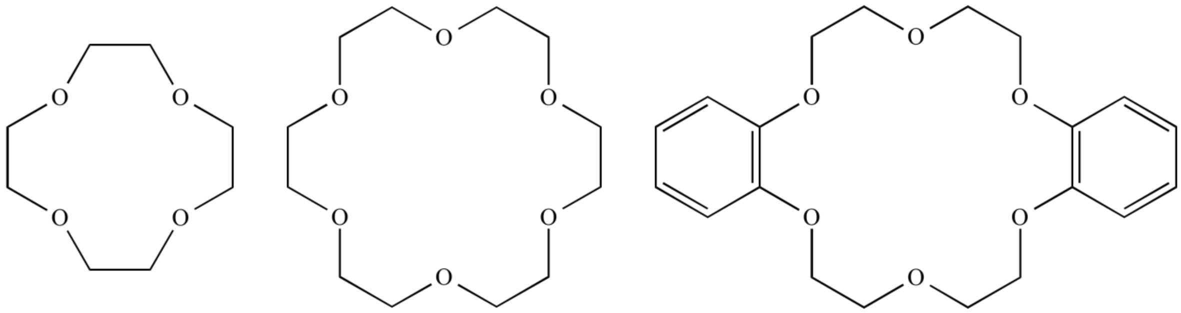
- Ethylene epoxide has many uses including generation of surfactants and detergents.
- Epoxy glues and structural materials are a result of epoxides reaction with amines.
- It is used as a stabilizer in materials like PVC. They are also used in manufacture of Epoxy resists that have low viscosity and without compromising strength and physical properties.

Epoxides are also used in things like insecticides, aerosols, resins and chemical intermediates.

Crown Ethers:

A series of cyclic ethers, featuring several oxygen atoms each separated by two carbon atoms. Called 'crown' ethers because their three-dimensional shape resembles a crown. Named as X-crown-Y, where X is the total number of atoms in the ring and Y is the total number of oxygen atoms. Crown ethers are notable because the exhibit selective cation binding (i.e., molecular recognition). For example, 12-crown-4 binds Li^+ more strongly than K^+, whereas 18-crown-6 binds K^+ more strongly than Li^+.

Structures



12-Crown-4 18-Crown-6 Dibenzo-18-crown-6

Some crown ethers.

Applications:

Crown ethers are **used to** bring inorganic catalysts into the organic phase and to increase the solubility of inorganic compounds in organic solvents to promote chemical reactions.

UNIT IV

THERMODYNAMICS-I

Definitions:

A primary goal of the study of thermochemistry is to determine the quantity of heat exchanged between a system and its surroundings. The **system** is the part of the universe being studied, while the **surroundings** are the rest of the universe that interacts with the system. A system and its surroundings can be as large as the rain forests in South America or as small as the contents of a beaker in a chemistry laboratory. The type of system one is dealing with can have very important implications in chemistry because the type of system dictates certain conditions and laws of thermodynamics associated with that system

System:

Open System

An **open system** is a system that freely exchanges *energy* and *matter* with its surroundings. For instance, when you are boiling soup in an open saucepan on a stove, energy and matter are being transferred to the surroundings through steam. The saucepan is an open system because it allows for the transfer of matter (for example adding spices in the saucepan) and for the transfer of energy (for example heating the saucepan and allowing steam to leave the saucepan).

Closed System

Putting a lid on the saucepan makes the saucepan a closed system. A **closed system** is a system that exchanges **only energy** with its surroundings, not matter. By putting a lid on the saucepan, matter can no longer transfer because the lid prevents matter from entering the saucepan and leaving the saucepan. Still, the saucepan allows energy transfer. Imagine putting the saucepan on a stove and heating it. The saucepan allows energy transfer as the saucepan heats up and heats the contents inside it. For example, when a lid is put a beaker, it becomes a closed system. This fog and mist is the steam which covers the sides of the container because it cannot escape the beaker due to the lid. The fact that the beaker is able to produce this steam means that the beaker allows for energy transfer. Thus, even though a closed system cannot allow matter transfer, it can still allow energy transfer.

The methods of energy transfer in a closed system are the same as those described for an open system above.

Isolated System

Now let's examine the type of system you have if you substituted a thermos for the saucepan. A thermos is used to keep things either cold or hot. Thus, a thermos does not allow for energy transfer. Additionally, the thermos, like any other closed container, does not allow matter transfer because it has a lid that does not allow anything to enter or leave the container. As a result, the thermos is what we call an isolated system. An **isolated system does not exchange energy or matter** with its surroundings. For example, if soup is poured into an insulated container (as seen below) and closed, there is no exchange of heat or matter. The fact that, in reality, a thermos is not perfect in keeping things warm/cold illustrates the difficulty in creating an truly isolated system. In fact, there are a few, if any, systems that exist in this world that are completely isolated systems.

Surrounding:

State of the System:

State of a function (system) is a condition of existence which is described by some measurable properties. For e.g.: water exists in three different states i.e. solid, liquid & gas depending upon the temperature at 1atm pressure.

The measurable properties of gaseous system are pressure, temperature, volume, mass or composition of substances. Any change in these properties will change the state of a system and these properties are called state variables.

Some state variables depend only on the initial and final state but not the path or process how it is carried out, and they are called state function.

If water is heated from 0°C to 50°C, then we say that the change in temperature is 50°C regardless the process how water is heated.

Intensive and Extensive Variables:

Extensive variable

Those state variables that depend upon the quality of matter are called extensive variables. For e.g.: mass, moles, volume, internal energy, enthalpy, entropy and free energy.

Intensive variable

Those state variables that depend upon the property of matter are called intensive variables. For e.g.: temperature, density, refractive index, etc.

Thermodynamic Processes:

Isothermal process
Any physical or chemical process in which the temperature remains constant during the state change is called isothermal process.

Here, $\Delta T=0$

Adbiatic process
Any physical or chemical process which takes place without flow of heat in or out of system during the state change is called adbiatic process.

Here, $\Delta Q=0$

Isobaric process
Any physical or chemical process in which the pressure of the system remains constant during the state change is called isobaric process.

Here, $\Delta P=0$

Isochoric process
Any physical or chemical process in which the volume remains constant during the state change is called isochoric process.

Here, $\Delta V=0$

Reversible and Irreversible:

Reversible process	Irreversible process
The process goes through infinite change so, it takes infinite time to complete.	The process goes through finite change so, it takes finite time to complete.
The process proceeds infinitesimally slowly maintaining the equation state.	This process is faster; the equilibrium state is maintained only at initial and final position of system.
During the state change it is in equilibrium state at all stages	Its is not equilibrium state during the stage change,driving force is always greaterthen opposing force.
This procsee only assumption impracticable	This procees is real and practicable

State and Path Functions:

State functions - definition

A physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. E.g pressure, volume, temperature.

Path functions - definition

Path functions are properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are heat and work.

State function - example

A state function describes the equilibrium state of a system. For example energy, enthalpy, internal and entropy are state quantities because they describe quantitatively an equilibrium state of a thermodynamic system, irrespective of how the system arrived in that state.

Work of Expansion at Constant Pressure and at Constant Volume:

First Law of Thermodynamics:

- Total energy in the universe remains constant.
- Energy can neither be created nor be destroyed but can be transferred from one form to another.

When Q amount of heat is supplied to the system, some part of it is used up to increase in its internal energy and remaining some part of it is used up for work done.

i.e. $Q=\Delta E+W$………………. (1)

If work is done by the system.

$Q=\Delta E-W$………………. (2)

If work is done on the system.

Where, Q= heat supplied

W=work done

ΔE=change in internal energy.

ΔE at constant volume

We have, from first law of thermodynamics;

$$Q=\Delta E+W$$

$$Q=\Delta E+P\Delta V$$

At constant volume, $\Delta V=0$

So, $Q=\Delta E$

It means, at constant volume condition, the total amount of heat supplied is equal to change Internal energy of system.

ΔE at adbiatic condition

We have, from first law of thermodynamics;

$$Q=\Delta E+W$$

At adbiatic condition, $Q=0$

So, $-W=\Delta E$

It means, at adbiatic condition, the work is done by utilizing the Internal energy of system.

Advantages of first law of thermodynamics

a. Total energy of the universe remains constant.

b. Different forms of energy are inter-convertible.

c. When one form of energy disappears, an equivalent amount of energy in another form appears.

Disadvantages of first law of thermodynamics

a. It doesn’t tell the extent and direction of the convertibility of one form of energy to another.

b. It doesn’t tell why chemical reactions do not proceed to completion.

c. It doesn’t tell why natural processes are unidirectional.

d. It doesn’t explain the feasibility and spontaneity of a process.

e. It says the equivalency of work and heat. But it has been observed that the work can be completely transformed into heat but heat cannot be transformed into work without permanent change in the system or surrounding which is not explained by the law.

Statement- Definition of Internal Energy (E):

A compound itself has a definite amount of energy which includes kinetic energy, potential energy, energy of atom, constituting molecules and chemical bond energy. The sum of these different forms of energy (molecules) is called internal energy denoted by E. Internal energy is the state function so, it depends upon initial and final state and also its absolute value cannot be determined however change can be measured.

Now, change in internal energy is given by:

$\Delta E=E_p-E_r$

Where, ΔE= change in Internal energy.

E_p= Internal energy of product.

E_r= Internal energy of reactant.

Sign convention of heat and work

1. Heat (q)

Case I:
When heat is absorbed by the system, $q = +ve$.

Case II:
When heat is released by the system, $q = -ve$.

2. Work (w)

Case I: (Work of Expansion)
When work is done by the system, $w = +ve$.

Case II: (Work of Compression)
When work is done on the system, $w = -ve$.

Enthalpy (H):

It is the sum of internal energy and product of pressure and volume.

i.e. $H=E+PV$…..(1)

Here, E, P & V all are state function so H is also the state function.

Being a state function it depends upon initial and final state and also its absolute value cannot be determined however change can be measured.

Now, $\Delta H=H_p-H_r$…………(2)

Where, H_p= enthalpy of product

H_r= Enthalpy of reactant

ΔH at constant pressure

We have, from first law of thermodynamics;

$$Q=\Delta E+W$$

$$Q=\Delta E+P\Delta V….(1)$$

Also, $H=E+PV……..(2)$

At constant pressure, $Q=Q_p$

So, equation (1) becomes,

$$Q_p=E_p-E_r+P(V_p-V_r)$$

$$Q_p=E_p+PV_p-(E_r+PV_r)$$

$$Q_p=H_p-H_r$$

$Q_p=\Delta H$

It means, heat of reaction at constant pressure is equal to change in enthalpy of reaction.

Heat Capacity:

When heat is absorbed by a body, the temperature of the body increases. And when heat is lost, the temperature decreases. The temperature of an object is the measure of the total kinetic energy of the particles that make up that object. So when heat is absorbed by an object this heat gets translated into the kinetic energy of the particles and as a result the temperature increases. Thus, the change in temperature is proportional to the heat transfer.

The formula **$q = n C \Delta T$** represents the heat q required to bring about a **ΔT** difference in temperature of one mole of any matter. The constant **C** here is called the molar heat capacity of the body. Thus, the molar heat capacity of any substance is defined as the amount of heat energy required to change the temperature of 1 mole of that substance by 1 unit. It depends on the nature, size, and composition of the system.

Relationship Between Cp And Cv:

- The molar heat capacity C, at constant pressure, is represented by **C_P**.
- At constant volume, the molar heat capacity C is represented by **C_V**.

In the following section, we will find how C_P and C_V are related, for an ideal gas.

The relationship between C_P and C_V for an Ideal Gas

From the equation $\mathbf{q = n\ C\ \Delta T}$, we can say:

At constant pressure P, we have

$\mathbf{q_P = n\ C_P \Delta T}$

This value is equal to the change in enthalpy, that is,

$\mathbf{q_P = n\ C_P \Delta T = \Delta H}$

Similarly, at constant volume V, we have

$\mathbf{q_V = n\ C_V \Delta T}$

This value is equal to the change in internal energy, that is,

$\mathbf{q_V = n\ C_V \Delta T = \Delta U}$

We know that for one mole (n=1) of an ideal gas,

$\mathbf{\Delta H = \Delta U + \Delta(pV\ )} = \Delta U + \Delta(RT) = \Delta U + R\ \Delta T$

Therefore, $\mathbf{\Delta H = \Delta U + R\ \Delta T}$

Substituting the values of ΔH and ΔU from above in the former equation,

$\mathbf{C_P \Delta T = C_V \Delta T + R\ \Delta T}$
$\mathbf{C_P = C_V + R}$
$\mathbf{C_P - C_V = R}$

Calculation of W:

Defined as mechanical energy equal to the product of the force (F) applied to an object and the distance (d) that the object is moved:

$$w = F \times d$$

Work, like heat, results from interaction between a system and its surroundings.

Chemical reactions can do two types of work:

Electrical work - When a reaction is used to drive an electric current through a wire.

e.g. a light bulb

Work of expansion - When a reaction causes a change in the volume of the system.

e.g. a gas pushing up a piston

The magnitude of work done when a gas expands is equal to the product of the pressure of the gas and the change in volume of the gas:

$$|w| = P\Delta V$$

Calculationof Q:

A form of energy associated with the random motion of the elementary particles in matter.

Heat capacity - The amount of heat needed to raise the temperature of a defined amount of a pure substance by one degree.

Specific heat - The amount of heat needed to raise the temperature of **one gram** of a substance by 1°C (or 1 K)

SI unit for specific heat is joules per gram^{-1} Kelvin^{-1} (J/g-K)

Calorie - The specific heat of water = 4.184 J/g-K

Molar heat capacity - The amount of heat required to raise the temperature of **one mole** of a substance by 1°C (or 1 K)

SI unit for molar heat capacity is joules per mole^{-1} Kelvin^{-1} (J/mol-K)

Btu (British thermal unit) - The amount of heat needed to raise the temperature of 1 lb water by 1°F.

Note: The specific heat of water (4.184 J/g-K) is very large relative to other substances. The oceans (which cover over 70% of the earth) act as a giant "heat sink," moderating drastic changes in temperature. Our body temperatures are also controlled by water and its high specific heat. Perspiration is a form of evaporative cooling which keeps our body temperatures from getting too high.

Thermochemistry:

Thermochemistry - A branch of thermodynamics which focuses on the study of heat given off or absorbed in a chemical reaction.

Temperature - An intensive property of matter; a quantitative measurement of the degree to which an object is either "hot" or "cold".

1. There are 3 scales for measuring temperature
    - **Fahrenheit** - relative
        - 32 F is the normal freezing point temperature of water; 212°F is the normal boiling point temperature of water.
    - **Celsius** (centigrade) - relative
        - 0°C is the normal freezing point temperature of water; 100°C is the normal boiling point temperature of water.
    - **Kelvin** - absolute
        - 0 K is the temperature at which the volume and pressure of an ideal gas extrapolate to zero.

Conversion Factors for Temperature

$$K = {}^{\circ}C + 273.15$$

$${}^{\circ}C = \frac{5}{9}({}^{\circ}F - 32)$$

$${}^{\circ}F = \frac{9}{5}({}^{\circ}C) + 32$$

Relationship between Enthalpy of Reaction at Constant Volume (qv) And At Constant Pressure (qp):

We define the enthalpy change (ΔH) as the heat of a process when pressure is held constant:

$\Delta H \equiv q$ at constant pressure

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line.

For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as

$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(\ell)\ \Delta H = -570$ kJ

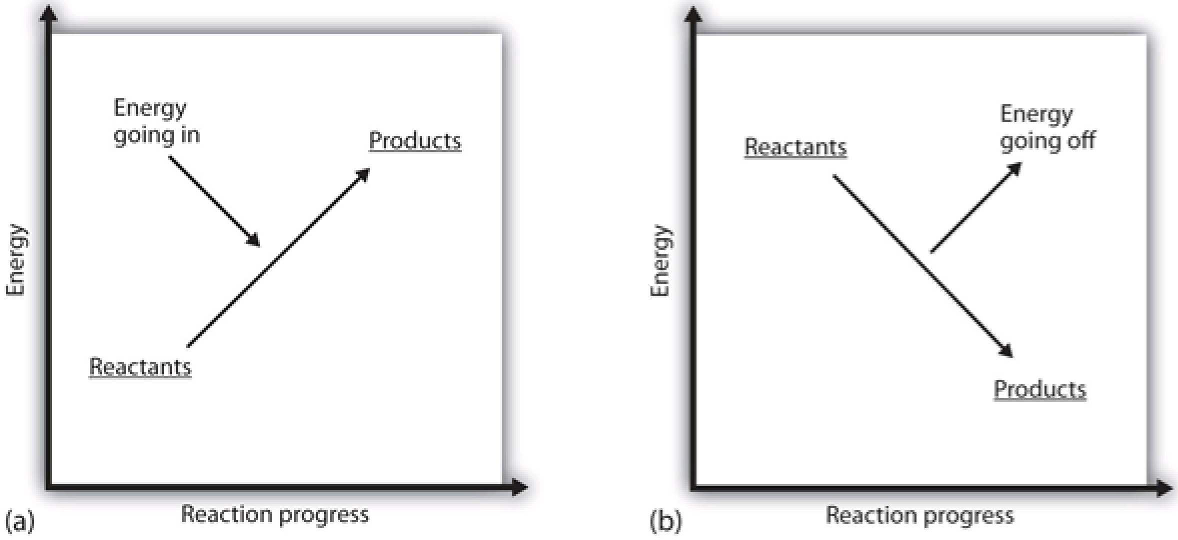
A chemical equation that includes an enthalpy change is called a thermochemical equation. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be endothermic, while a chemical reaction that has a negative ΔH is said to be exothermic.

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) in Figure "Reaction Energy": the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) in Figure "Reaction Energy". If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

Figure for Reaction Energy



(a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy).

(b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).

Temperature Dependence of Heat of Reaction:

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH=C_pdT \qquad (1)$$

And so for a temperature change from T_1 to T_2

$$\Delta H=\int_{T_2T_2}C_pdT \qquad (2)$$

The above equation is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H=C_p\Delta T \qquad (3)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 2

. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T)=a+bT+cT_2 \qquad (4)$$

After combining Equations 4 and 2, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H=\int_{T_2T_1}(a+bT+cT_2)dT \qquad (5)$$

Solving the definite integral yields

$$\Delta H=[aT+b2T_2-cT]_{T_2T_1}=a(T_2-T_1)+b2(T_{22}-T_{21})-c(1T_2-1T \qquad (6)(\ 7)$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table

Kirchoff’s Equation:

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

$$cp=\Delta H\Delta T \qquad (1)$$

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities.

The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants.

A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

$$HTf=HTi+\int TfTicpdT \qquad (2)$$

If the heat capacity is temperature independent over the temperature range, then Equation 1

can be approximated as

$$HTf=HTi+cp(Tf-Ti) \qquad (3)$$

With cp is the (assumed constant) heat capacity and

HTi and HTf are the enthalpy at the respective temperatures.

Equation 3 can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

Bond Energy and its Calculation From Thermochemical Data:

Bond energy of a bond is amount of energy required to break 1 mole of a bond in gaseous state or energy released when one mole of a bond is formed in gaseous state.

In terms of bond energy,

Heat reaction = Heat absorbed – Heat released = bond energies of reactants – bond energies of products

Estimate the enthalpy change for the reaction

H_2 (g) + Cl_2 (g) → 2HCl (g)

Given bond energy of H – H = 435 KJ $mole^{-1}$

Bond energy of Cl-Cl = 243 $KJmole^{-1}$

Bond energy of H-Cl = 430 $KJmole^{-1}$

Sol:

The amount of energy released during formation of 2moles of H-Cl bond = 2 × 430 = 860 KJ

H reaction = Energy absorbed – Energy released

= 618 – 860

= -182 KJ

Calculate the enthalpy change for the hydrogenation of ethane gas.

$CH_2 = CH_2$ (g) + H_2 (g) → $CH_3 – CH_3$ (g)

Given, bond energy of H -H bond = 435 KJ $mole^{-1}$

Bond energy of C – H bond = 413 KJ $mole^{-1}$

Bond energy of C -C bond = 347 KJ $mole^{-1}$

Bond energy of C=C bond = 615 KJ $mole^{-1}$

The amount of energy absorbed during reaction

= 413 × 4 + 615 + 435

= 2702 KJ

Energy released during reaction

= 6 × 413 + 347

= 2825 KJ

H reaction = 2825 – 2702 KJ = -123 KJ

Integral and Differential Heats of Solution:

Dilution:

When one mole of a substance is dissolved in a specified quantity of solvent in a large number of steps the enthalpy change per mole of solid for each step is called the differential heat of solution. Sometimes it is desirable to define another enthalpy term known as **enthalpy of dilution.** The heat of dilution is the difference between two integral heats of solutions.

Considering example**:** If some ammonium chloride or glucose is added to water in a test tube the tube becomes cooler. On the other hand if some solid NaOH is added to the test tube the water becomes quite warm. These are examples of a common experience that when solids are dissolved in water heat is either absorbed or evolved.

$Na^+ OH^- (s) + H_2O (l) \rightarrow Na^+ (aq) + OH^- (aq)$; $\Delta H = -40$ kJ mol^{-1}

$NH_4^+ NO_3^- (s) + H_2O (l) \rightarrow NH_4^+ (aq) + NO_3^- (aq)$; $\Delta H = +26$ kJ mol^{-1}

The heat of a solution of NaOH in water, the heat of solution of 1.0 mole of NaOH in 5 moles of water and in 200 moles of water are respectively – 37.8 and -42.3 kJ. Thus, in the above example of enthalpy of solution of NaOH the difference between the two values, – 4.5 kJ would be the enthalpy of dilution.

On many occasions it is essential to know the enthalpy of solution at infinite dilution. If we keep on diluting a solution by gradual addition of the solvent there will be heat change at each dilution. Finally a stage will come when any further dilution produces no thermal change. This stage is called the state of infinite dilution. The enthalpy of solution at infinite dilution is defined as:

"The enthalpy change when one mole of a substance is dissolved in such a large volume of solvent so that any further dilution produces no thermal effect".

The integral heat of solution reaches a limiting value at infinite dilution. Thus if 1.0 mole of HC1 is dissolved in a large volume of water so that no heat change is observed when more water is added one can write

$HCl (g) + aq \rightarrow HC1(aq)$; $\Delta H^0 = -75.1$ kJ

UNIT V

CHEMICAL KINETICS

Rate of reaction:

The rate of reaction or reaction rate is the speed at which reactants are converted into products. When we talk about chemical reactions, it is a given fact that rate at which they occur varies by a great deal. Some chemical reactions are nearly instantaneous, while others usually take some time to reach the final equilibrium.

This article aims to help students learn about and understand what exactly is the rate of reaction for a given chemical compound.

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As per the general definition, the speed with which a reaction takes place is referred to as the rate of a reaction.

For example, wood combustion has a high reaction rate since the process is fast and rusting of iron has a low reaction rate as the process is slow.

Rate equation:

Let’s take a traditional chemical reaction.

a A + b B → p P + q Q

Capital letters (A&B) denote reactants and the (P&Q) denote products, while small letters (a,b,p,q) denote Stoichiometric coefficients.

As per IUPAC’s Gold Book, the rate of reaction **r** occurring in a closed system without the formation of reaction intermediates under isochoric conditions is defined as:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{p}\frac{d[\mathrm{P}]}{dt} = \frac{1}{q}\frac{d[\mathrm{Q}]}{dt}$$

Here, the negative sign is used to indicate the decreasing concentration of the reactant.

Order and Molecularity of Reaction:

The molecularity of a reaction refers to the number of atoms, molecules, or ions which must undergo a collision with each other in a short time interval for the chemical reaction to proceed. The key differences between molecularity and reaction order are tabulated below.

Molecularity	**Order of Reaction**
It is always a whole number	It can be a whole number or a fraction.
It can be determined from the balanced chemical equation	It must be determined experimentally
Is only applicable in simple reactions	The reaction order is applicable in all chemical reactions

It can be noted that when the order of reaction is a fraction, the reaction is generally a chain reaction or follows some other complex mechanism. An example of a chemical reaction with a fractional reaction order is the pyrolysis of acetaldehyde.

Rate Laws:

The rate law (also known as the rate equation) for a chemical reaction is an expression that provides a relationship between the rate of the reaction and the concentrations of the reactants participating in it.

Expression

For a reaction given by:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

Where a, b, c, and d are the stoichiometric coefficients of the reactants or products, the rate equation for the reaction is given by:

$$\mathbf{Rate \propto [A]^x[B]^y \Rightarrow Rate = k[A]^x[B]^y}$$

Where,

- [A] & [B] denote the concentrations of the reactants A and B.
- x & y denote the partial reaction orders for reactants A & B (which may or may not be equal to their stoichiometric coefficients a & b).
- The proportionality constant ‘k’ is the rate constant of the reaction.

Reaction Orders

The sum of the partial orders of the reactants in the rate law expression gives the overall order of the reaction.

If Rate = $k[A]^x[B]^y$; overall order of the reaction (n) = $x+y$

The order of a reaction provides insight into the change in the rate of the reaction that can be expected by increasing the concentration of the reactants. For example:

- If the reaction is a zero-order reaction, doubling the reactant concentration will have no effect on the reaction rate.
- If the reaction is of the first order, doubling the reactant concentration will double the reaction rate.
- In second-order reactions, doubling the concentration of the reactants will quadruple the overall reaction rate.
- For third-order reactions, the overall rate increases by eight times when the reactant concentration is doubled.

Rate Constants:

Rearranging the rate equation, the value of the rate constant 'k' is given by:

$k = Rate/[A]^x[B]^y$

Therefore, the units of k (assuming that concentration is represented in $mol.L^{-1}$ or M and time is represented in seconds) can be calculated via the following equation.
$k = (M.s^{-1})*(M^{-n}) = M^{(1-n)}.s^{-1}$

The units of the rate constants for zero, first, second, and n^th-order reactions are tabulated below.

Reaction Order	**Units of Rate Constant**
0	$M.s^{-1}$ (or) $mol.L^{-1}.s^{-1}$
1	s^{-1}
2	$M^{-1}.s^{-1}$ (or) $L.mol^{-1}.s^{-1}$
N	$M^{1-n}.s^{-1}$ (or) $L^{(-1+n)}.mol^{(1-n)}.s^{-1}$

Differential Rate Equations

Differential rate laws are used to express the rate of a reaction in terms of the changes in reactant concentrations (d[R]) over a small interval of time (dt). Therefore, the differential form of the rate expression provided in the previous subsection is given by:

$$-d[R]/dt = k[A]^x[B]^y$$

Differential rate equations can be used to calculate the instantaneous rate of a reaction, which is the reaction rate under a very small time interval. It can be noted that the ordinary rate law is a differential rate equation since it offers insight into the instantaneous rate of the reaction.

Integrated Rate Equations

Integrated rate equations express the concentration of the reactants in a chemical reaction as a function of time. Therefore, such rate equations can be employed to check how long it would take for a given percentage of the reactants to be consumed in a chemical reaction. It is important to note that reactions of different orders have different integrated rate equations.

Integrated Rate Equation for Zero-Order Reactions

The integrated rate equation for a zero-order reaction is given by:

$$kt = [R_0] - [R] \text{ (or) } k = ([R_0] - [R])/t$$

Where,

- $[R_0]$ is the initial concentration of the reactant (when $t = 0$)
- $[R]$ is the concentration of the reactant at time ‘t’
- k is the rate constant

Derivation of first order rate constant:

The integrated rate law for first-order reactions is:

$$kt = 2.303\log([R_0]/[R]) \text{ (or) } k = (2.303/t)\log([R_0]/[R])$$

Integrated Rate Equation for Second-Order Reactions

For second-order reactions, the integrated rate equation is:

$$kt = (1/[R]) - (1/[R_0])$$

Example

For the reaction given by $2NO + O_2 \rightarrow 2NO_2$, The rate equation is:

Rate = $k[NO]^2[O_2]$

Find the overall order of the reaction and the units of the rate constant.

The overall order of the reaction = sum of exponents of reactants in the rate equation = 2+1 = 3

The reaction is a third-order reaction. Units of rate constant for 'nth' order reaction = $M^{(1-n)}.s^{-1}$

Therefore, units of rate constant for the third-order reaction = $M^{(1-3)}.s^{-1} = M^{-2}.s^{-1} = L^2.mol^{-2}.s^{-1}$

Example

For the first-order reaction given by $2N_2O_5 \rightarrow 4NO_2 + O_2$ the initial concentration of N_2O_5 was 0.1M (at a constant temperature of 300K). After 10 minutes, the concentration of N_2O_5 was found to be 0.01M. Find the rate constant of this reaction (at 300K).

From the integral rate equation of first-order reactions:

$k = (2.303/t)\log([R_0]/[R])$

Given, t = 10 mins = 600 s

Initial concentration, $[R_0]$ = 0.1M

Final concentration, $[R]$ = 0.01M

Therefore, rate constant, $k = (2.303/600s)\log(0.1M/0.01M) = 0.0038\ s^{-1}$

The rate constant of this equation is $0.0038\ s^{-1}$

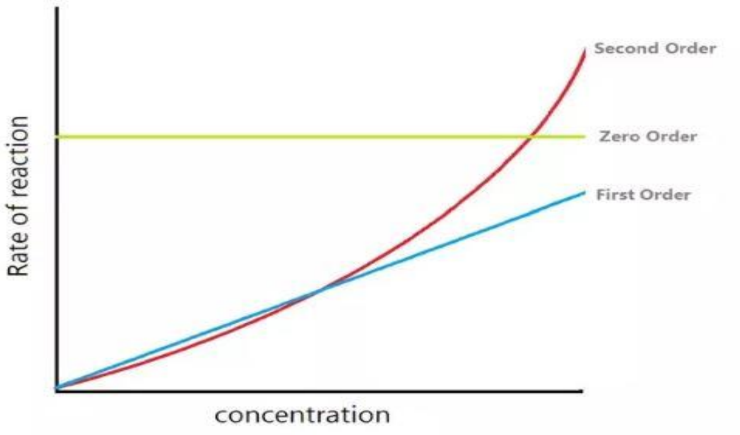
Characteristics of zero order:

- The rate of reaction is independent of the concentration of the reactants in these reactions.
- A change in the concentration of the reactants has no effect on the speed of the reaction
- Examples of these types of reactions include the enzyme-catalyzed oxidation of CH_3CH_2OH (ethanol) to CH_3CHO (acetaldehyde).

First order reaction:

- The rates of these reactions depend on the concentration of only one reactant, i.e. the order of reaction is 1.

- In these reactions, there may be multiple reactants present, but only one reactant will be of first-order concentration while the rest of the reactants would be of zero-order concentration.
- Example of a first-order reaction: $\mathbf{2H_2O_2 \rightarrow 2H_2O + O_2}$



Pseudo-First Order Reactions

- In a pseudo-first order reaction, the concentration of one reactant remains constant and is therefore included in the rate constant in the rate expression.
- The concentration of the reactant may be constant because it is present in excess when compared to the concentration of other reactants, or because it is a catalyst.
- Example of a pseudo-first order reaction: $\mathbf{CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH}$ (this reaction follows pseudo-first order kinetics because water is present in excess).

second order reactions:

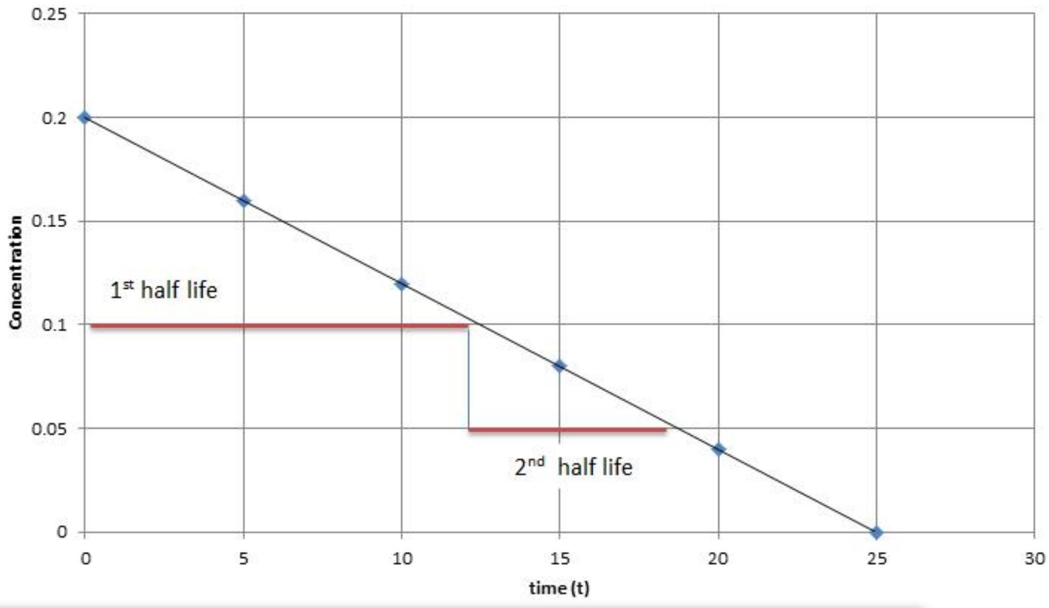
- When the order of a reaction is 2, the reaction is said to be a second-order reaction.
- The rate of these reactions can be obtained either from the concentration of one reactant squared or from the concentration of two separate reactants.
- The rate equation can correspond to $\mathbf{r = k[A]^2}$ or $\mathbf{r = k[A][B]}$
- Example of a second-order reaction: $\mathbf{NO_2 + CO \rightarrow NO + CO_2}$

Derivation of time for half change (t1/2) with examples:

The half-life of a reaction, $t_{1/2}$, is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration. The concepts of half life plays a key role in the administration of drugs into the target, especially in the elimination phase, where half life is used to determine how quickly a drug decrease in the target after it has been absorbed in the unit of time (sec, minute, day,etc.) or elimination rate constant ke (minute^{-1}, hour^{-1}, day^{-1},etc.). It is important to note that the half-life is varied between different type of reactions.

Zero order kinetics

In zero-order kinetics, the rate of a reaction does not depend on the substrate concentration. In other words, saturating the amount of substrate does not speed up the rate of the reaction. Below is a graph of time (t) vs. concentration [A] in a zero order reaction, several observation can be made: the slope of this plot is a straight line with negative slope equal negative k, the half-life of zero order reaction decrease as the concentration decrease.



We learn that the zero order kinetic rate law is as followed, where [A] is the current concentration, $[A]_0$ is the initial concentration, and k is the reaction constant and t is time:

$$[A]=[A]_0-kt \qquad (1)$$

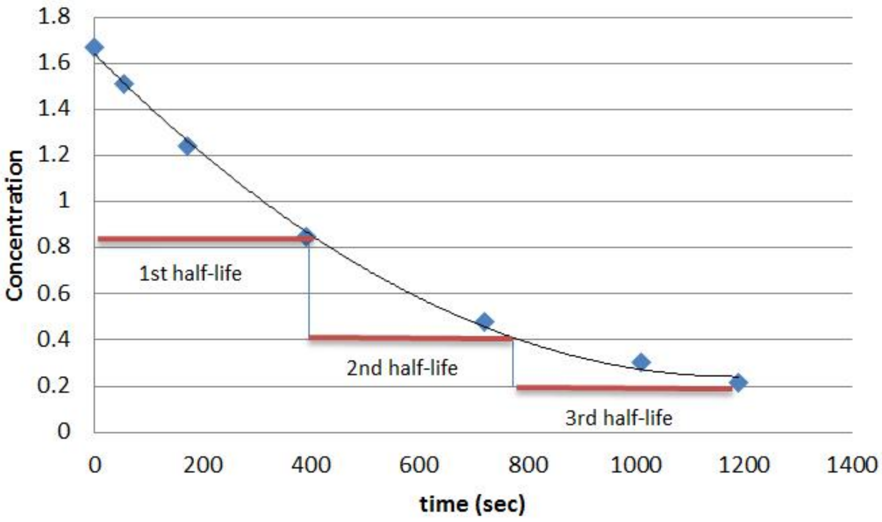
In order to find the half life we need to isolate t on its own, and divide it by 2. We would end up with a formula as such depict how long it takes for the initial concentration to dwindle by half:

$$t_{1/2}=[A]_0 2k \qquad (2)$$

The $t_{1/2}$ formula for a zero order reaction suggests the half-life depends on the amount of initial concentration and rate constant.

First Order Kinetics

In First order reactions, the graph represents the half-life is different from zero order reaction in a way that the slope continually decreases as time progresses until it reaches zero. We can also easily see that the length of half-life will be constant, independent of concentration. For example, it takes the same amount of time for the concentration to decrease from one point to another point.



In order to solve the half life of first order reactions, we recall that the rate law of a first order reaction was:

$[A]=[A]_0 e^{-kt}$ (3)

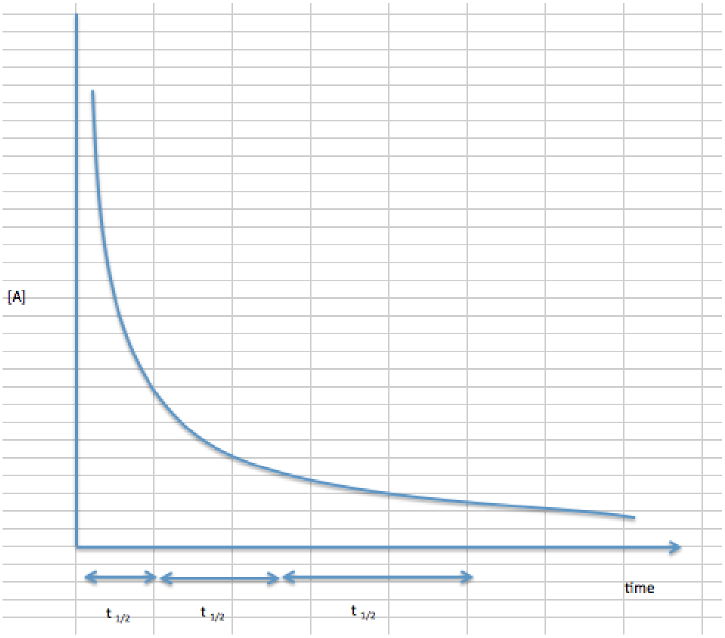
To find the half life we need to isolate t and substitute [A] with $[A]_0/2$, we end up with an equation looking like this:

$t_{1/2}=\ln 2/k \approx 0.693k$ (4)

The formula for $t_{1/2}$ shows that for first order reactions, the half-life depends solely on the reaction rate constant, k. We can visually see this on the graph for first order reactions when we note that the amount of time between one half life and the next are the same. Another way to see it is that the half life of a first order reaction is independent of its initial concentration.

Second Order Reactions

Half-life of second order reactions shows concentration [A] vs. time (t), which is similar to first order plots in that their slopes decrease to zero with time. However, second order reactions decrease at a much faster rate as the graph shows. We can also note that the length of half-life increase while the concentration of substrate constantly decreases, unlike zero and first order reaction.



In order to solve for half life of second order reactions we need to remember that the rate law of a second order reaction is:

$1/[A]=kt+1/[A]_0$ (5)

As in zero and first order reactions, we need to isolate T on its own:

$t_{1/2}=1/k[A]_0$ (6)

This replacement represents half the initial concentration at time, t (depicted as $t_{1/2}$). We then insert the variables into the formula and solve for $t_{1/2}$. The formula for $t_{1/2}$ shows that for second order reactions, the half-life only depends on the initial concentration and the rate constant.

Methods of Determination of Order of Reactions:

There are several different methods which can be followed in order to determine the reaction order. Some of these methods are described in this subsection.

Initial Rates Method

- First, the natural logarithm form of the power-law expression is obtained. It is given by: **ln r = ln k + x.ln[A] + y.ln[B] + ….**
- The partial order corresponding to each reactant is now calculated by conducting the reaction with varying concentrations of the reactant in question and the concentration of the other reactants kept constant.
- If the partial order of A is being determined, the power-law expression of the rate equation now becomes **ln r = x.ln[A] + C**, where C is a constant.

- A graph is now plotted by taking 'ln r' as a function of ln[A], the corresponding slope is the partial order, given by x.

Integral Method

- The order of reaction obtained from the initial rates method is usually verified using this method.
- The measured concentrations of the reactants are compared with the integral form of the rate law.
- For example, the rate law for a first-order reaction is verified if the value for ln[A] corresponds to a linear function of time (integrated rate equation of a first-order reaction: $\ln[A] = -kt + \ln[A]_0$).

Differential Method

- This method is the easiest way to obtain the order of reaction
- First, the rate expression of the reaction is written ($r = k[A]^x[B]^y..$)
- The sum of the exponents x+y+… gives the final value of the reaction order.

Apart from these methods, there exist other ways to obtain the reaction order, such as the method of flooding in which the concentration of a single reactant is measured when all the other reactants are present in huge excess.

Experimental Methods:

Colorimetry Experimental Methods:

Calorimetry is the science associated with determining the changes in energy of a system by measuring the heat exchanged with the surroundings.

Calorimetry labs are frequently performed in order to determine the heat of reaction or the heat of fusion or the heat of dissolution or even the specific heat capacity of a metal.

A calorimeter is a device used to measure the quantity of heat transferred to or from an object. Most students likely do not remember using such a *fancy piece of equipment* known as a calorimeter. Fear not; the reason for the lack of memory is not a sign of early Alzheimer's. The more sophisticated cases include a lid on the cup with an inserted thermometer and maybe even a stirrer.

Coffee Cup Calorimetry

So how can such simple equipment be used to measure the quantity of heat gained or lost by a system? We have learned on the previous page, that water will change its temperature when it gains or loses energy. And in fact, the quantity of energy gained or lost is given by the equation

$$Q = m_{water} \cdot C_{water} \cdot \Delta T_{water}$$

where C_{water} is 4.18 J/g/°C. So if the mass of water and the temperature change of the water in the coffee cup calorimeter can be measured, the quantity of energy gained or lost by the water can be calculated.

The assumption behind the science of calorimetry is that the energy gained or lost by the water is equal to the energy lost or gained by the object under study. So if an attempt is being made to determine the specific heat of fusion of ice using a coffee cup calorimeter, then the assumption is that the energy gained by the ice when melting is equal to the energy lost by the surrounding water. It is assumed that there is a heat exchange between the iceand the water in the cup and that no other objects are involved in the heat exchanged. This statement could be placed in equation form as

$$Q_{ice} = - Q_{surroundings} = -Q_{calorimeter}$$

The heat exchanged in a calorimeter should be between the water and the system; heat should not be lost to the surrounding air.

The role of the Styrofoam in a coffee cup calorimeter is that it reduces the amount of heat exchange between the water in the coffee cup and the surrounding air. The value of a lid on the coffee cup is that it also reduces the amount of heat exchange between the water and the surrounding air. The more that these other heat exchanges are reduced, the more true that the above mathematical equation will be. Any error analysis of a calorimetry experiment must take into consideration the flow of heat from system to calorimeter to other parts of the *surroundings*. And any design of a calorimeter experiment must give attention to reducing the exchanges of heat between the calorimeter contents and the *surroundings*.

Polarimetry Experimental Methods:

A **polarimeter** is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance.

Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the angle of rotation. The angle of rotation is basically known as observed angle.

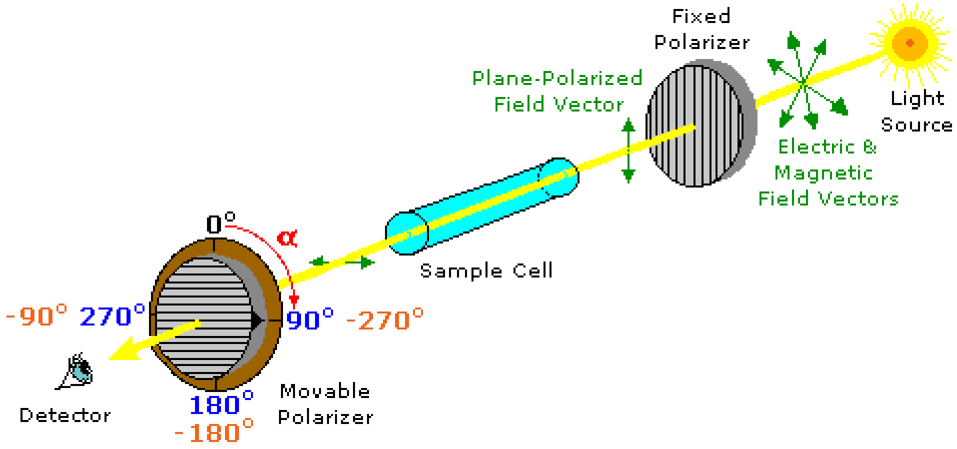
Because many optically active chemicals such as tartaric acid, are stereoisomers, a polarimeter can be used to identify which isomer is present in a sample – if it rotates polarized light to the left, it is a levo-isomer, and to the right, a dextro-isomer. It can also be used to measure the ratio of enantiomers in solutions.

The optical rotation is proportional to the concentration of the optically active substances in solution. Polarimetry may therefore be applied for concentration measurements of enantiomer-pure samples. With a known concentration of a sample, polarimetry may also be applied to determine the specific rotation (a physical property) when characterizing a new substance.

By the same token, if the specific rotation of a sample is already known, then the concentration and/or purity of a solution containing it can be calculated.

Most automatic polarimeters make this calculation automatically, given input on variables from the user.

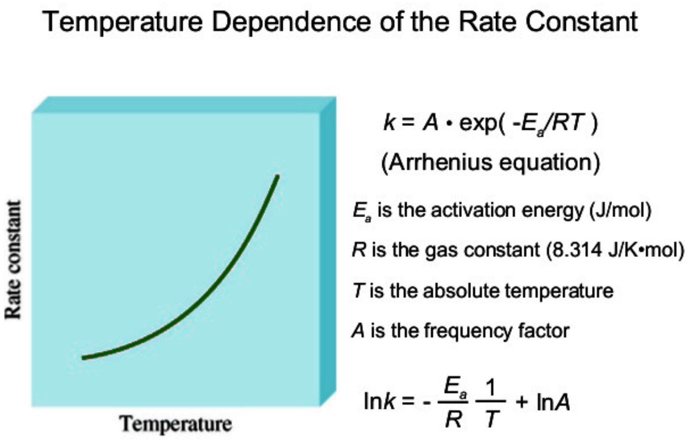
Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter**, shown in the diagram below.



Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer ($\alpha = 0^{o}$). If the analyzer is turned 90º to the plane of initial polarization, all the light will be blocked from reaching the detector.

Effect of Temperature on Reaction Rate:

Temperature is one of the parameters that can affect the rate of a chemical reaction considerably. We have often seen milk boiling on a gas stove. The rate at which a specific quantity of milk boils depends on the flame of the stove. If the flame height is maximum, the milk boils in less time and if the flame height is minimum, the milk takes more time to boil. Here the flame height resembles temperature.



If the temperature is high, the milk attains its boiling point in less time and if the temperature is low, the milk takes more time to attain its boiling point. The boiling of milk is not the only reaction that gets affected by temperature. Most of the chemical reactions show a change in their reaction rate with the varying in temperature.

It has been observed that the rate constant for a chemical reaction gets doubled for every 10^{o}C rise in temperature. Until 1889, there was no fixed way to physically measure the temperature dependence of the rate of a chemical reaction. In 1889, Svante Arrhenius extended the work of J.H van't Hoff and proposed an equation that related temperature and the rate constant for a reaction quantitatively. The proposed equation was named as Arrhenius Equation.

Arrhenius Equation:

Here is the Arrhenius Equation on the temperature dependence of the rate of a chemical reaction.

$k=Ae_{-EaRT}$

Where,

k=rateconstantofthereaction
A=ArrheniusConstant
E$_a$=ActivationEnergy forthereaction(inJoulesmol^{-1})
R=UniversalGasConstant
T= Temperature in absolute scale (in kelvins)

We knew that the rates of reaction increase with an increase in temperature but it was not known on how to predict the relation between temperature and reaction rates quantitatively. Arrhenius Equation has enabled us to overcome this problem. It is an empirical relation that is used to model the variation of the rate constant with the temperature, that in turn gives information about the rates of chemical reactions at different temperatures.

Concept of Activation Energy:

Activation energy is defined as the minimum amount of extra energy required by a reacting molecule to get converted into product. It can also be described as the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation.

SI Unit of Activation Energy

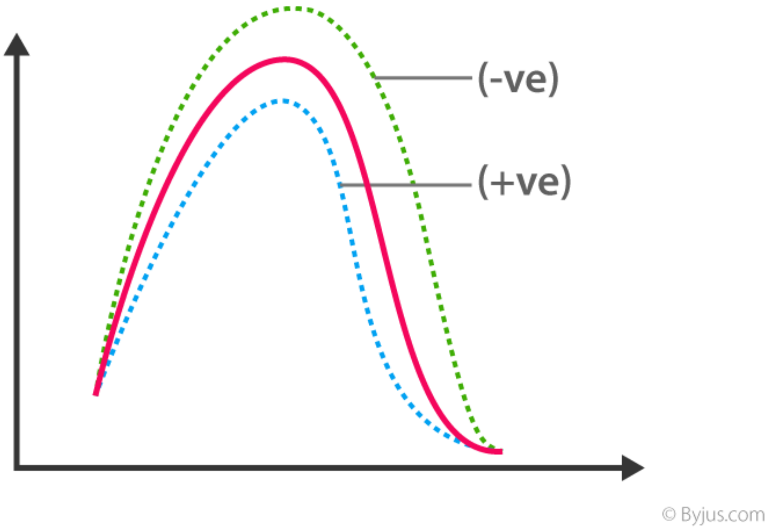
Activation energy is denoted by E_a. It is usually measured in joules (J) and or kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol).
Activation energy depends on two factors.

1. Nature of Reactants

In the case of ionic reactant, the value of (E_a) will be low because there is an attraction between reacting species. While in the case of covalent reactant the value of E_a will be high because energy is required to break the older bonds.

2. Effect of Catalyst

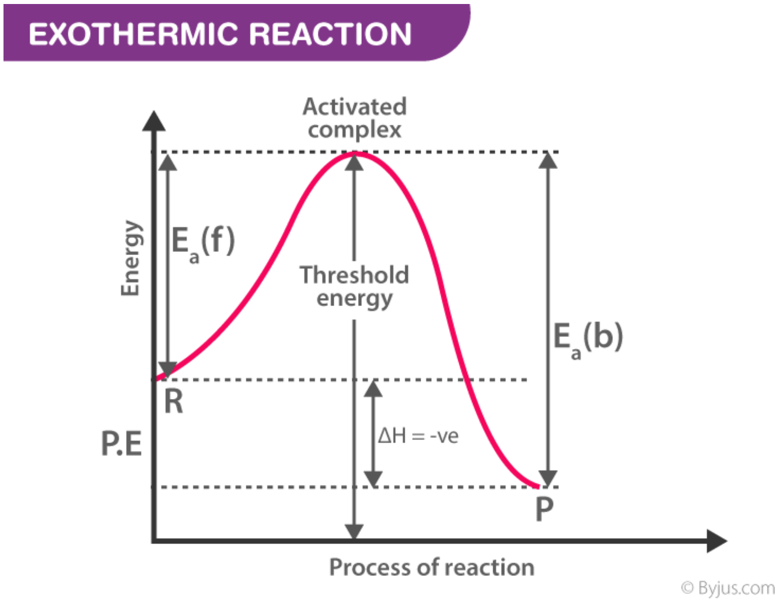
Positive catalyst provides such an alternate path in which the value of E_a will be low, while the negative catalyst provides such an alternate path in which the value of E_a will be high.



Note: Activation energy does not depend upon the temperature, pressure, volume, concentration, or coefficients of reactant.

Activation Energy Examples

Exothermic Reaction



Activation energy for Forward reaction $(E_a)_f$

Activation energy for Forward reaction $(E_a)_b$

$$(E_a)_f < (E_a)_b$$

$(ROR)_f > (ROR)_b$

$\triangle H = (E_a)_f - (E_a)_b$

$\triangle H$ = -ve value

$(E_a)_f = \triangle H$ Only one can be possible for Exothermic Reaction

$(E_a)_f > \triangle H$

$(E_a)_f < \triangle H$

Endothermic Reaction

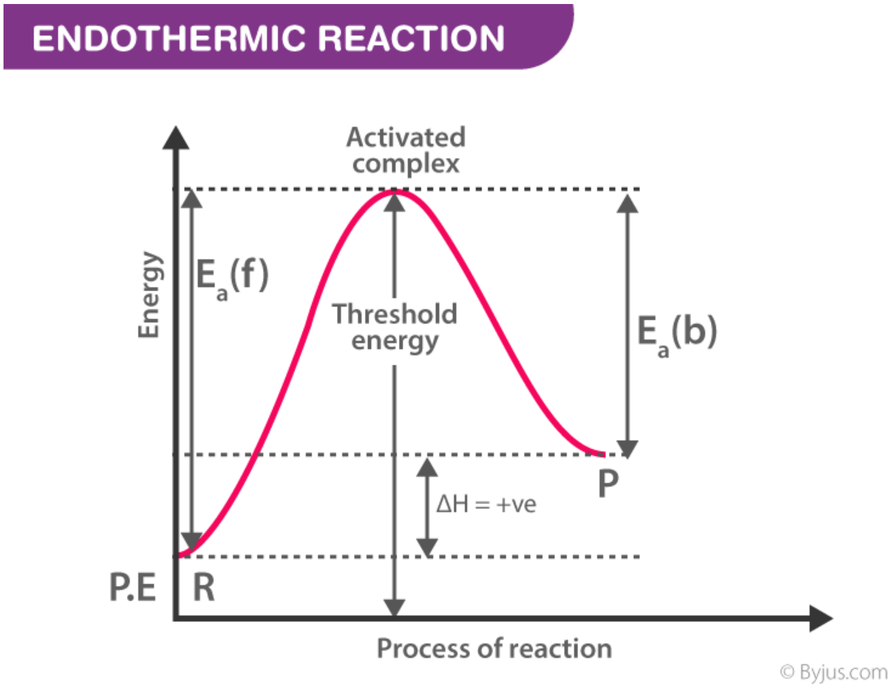
$(E_a)_f > (E_a)_b$

$(ROR)_f < (ROR)_b$

$\triangle H = (E_a)_b - (E_a)_f$

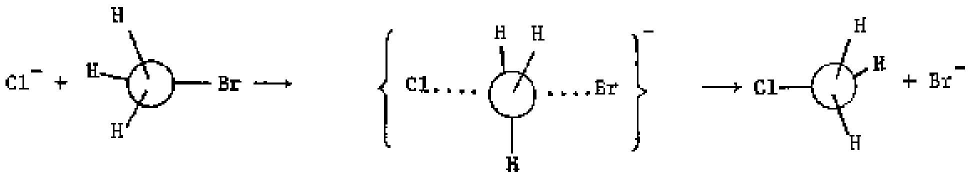
$\triangle H$ = +ve value

$(E_a)_f > \triangle H$ (Always)………..universal



Energy Barrier:

During the course of a reaction considerable redistribution of electrons may occur. Consider, for example, the reaction of CH_3Br with Cl^- in water at 298K.



As the bimolecular reaction occurs:

(i) There is angle bending: the initially pyramidal CH_3 grouping become planar;

(ii) There is bond-making and breaking: a partial CBr bond is weakened. The energy released by the formation of the partial CCl bond will not fully compensate for the other two (endothermic) changes and yet there is no lower energy pathway from reactants to products.

The reactants can get to the point of highest potential energy (the "activated complex" or "transition state" - in curly braces above) only if they initially have sufficient kinetic energy to turn into the potential energy of the activated complex.

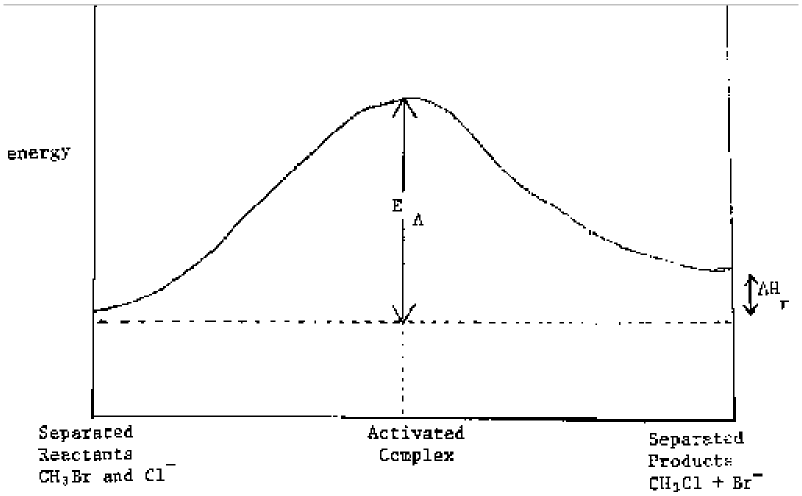
The activated complex can not be isolated; it is that arrangement of reactants which can proceed to products without further input of energy.

It is often useful to make a schematic plot of the total energy (enthalpy) of the combined reactant molecules during the various stages of the chemical reaction. The points on the plot which we can pinpoint are:

(i) the difference between the average energy of the products and the average energy of the reactants, $H_{reaction}$ (~ + 25 kJ mol$^-$ for $CH_3Br + Cl^-$) and

(ii) the activation energy (obtained experimentally; 103 kJ mol$^-$ for $CH_3Br + Cl^-$).

If we assume the total energy varies smoothly with the course of the reaction we obtain the following "energy profile":



It is important to note that there will be more than one way for the reactants to interact and so pass to the products. However, there can only be one minimum energy pathway and essentially all of the reaction will occur via this pathway.

Arrhenius equation:

An elementary bimolecular reaction originates from a collision between two reactants. Whether or not a collision results in a chemical reaction is determined by the energy of the reactants and their orientation. The total energy of the two reactants must be in excess of the activation energy, E_a, and the reactants must be in a favorable orientation for the chemical reaction to occur. While there are many different orientations possible for the collisions, usually not all of them will result in a chemical reaction. For most reactions, if the orientation is not correct, the reactants will bounce off of each other without a chemical reaction.

Reaction Rate

The rate of a bimolecular reaction, between the reactants A and B is expressed as,

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

where k is the reaction's rate constant and [A] and [B] are the reactants' concentrations. The reaction rate represents the "speed" of the chemical reaction and is equal to the magnitude of the change in the concentration of A or B per unit time. Thus, the reaction rate has units of concentration/time. Because one B molecule reacts for every A molecule, the loss rates of A and B are equal. The activation energy is illustrated in the following diagram. The difference in the activation energies for the forward and reverse reactions equals the change in the internal energy for the chemical reaction; i.e.,

$$\Delta E_{rxn}=E_{fa}-E_{ra}$$

Theories of Reaction Rates

Collision Theory:

The collision theory explains that gas-phase chemical reactions occur when molecules collide with sufficient kinetic energy. The collision theory is based on the kinetic theory of gases; therefore only dealing with gas-phase chemical reactions are dealt with. Ideal gas assumptions are applied. Furthermore, we also are assuming:

1. All molecules are traveling through space in a straight line.
2. All molecules are rigid spheres.
3. The reactions concerned are between only two molecules.
4. The molecules need to collide.

Ultimately, the collision theory of gases gives the **rate constant** for bimolecular gas-phase reactions; it is equal to the rate of successful collisions. The rate of successful collisions is proportional to the *fraction of successful collisions* multiplied by the overall *collision frequency*.

Derivation of Rate Constant of Bimolecular Reaction:

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Failure of Collision Theory:

The following are the drawbacks of collision theory.

- This theory does not advance any explanation for the abnormally high rates that are observed sometimes.
- This theory cannot be applied to reversible reactions with complete success.
- It does not take into account the fact that proper molecule orientation is the requirement for a chemical reaction to occur. Active collision does not occur due to lack of proper orientation and therefore the experimentally observed frequency is less than determined based on the theory of collision.
- The theory of collision states that the reaction frequency is proportional to the total number of collisions per cc per second.
- It does not take into account the fast reactions where reactant molecules react despite having much less energy than the activation energy. These reactions are described by quantum mechanics, which means the reaction happens as a result of electrons being exchanged between reactant molecules.

Lindemann's theory of Unimolecular Reaction:

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step.

The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

General Mechanism

The schematic reaction $A+M\rightarrow P$

is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of *A*

$A+M\rightleftharpoons A_*+M$(29.6.1)

with

forward activation reaction rate: k_1

reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of *A*

$A\rightarrow_{k_2}P$(29.6.2)

with

forward reaction rate: k_2