

INTRODUCTION TO ORGANIC CHEMISTRY



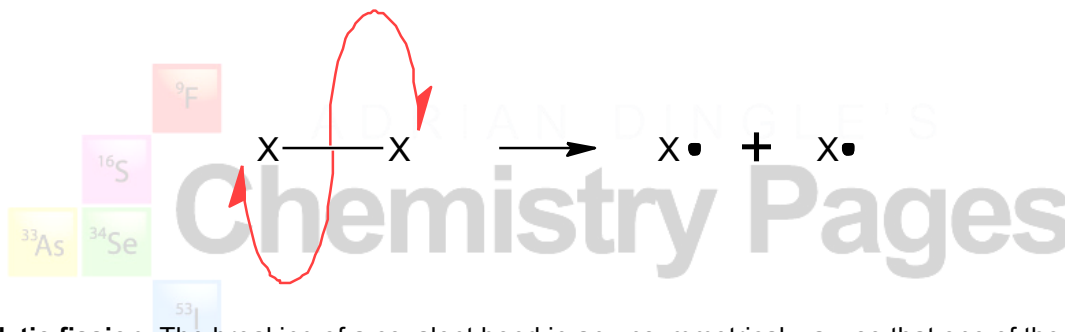
## UNIT 03: Mechanisms

A mechanism describes the detail of a chemical reaction in terms of the bonds broken and the bonds made. Since covalent bonds are shared electrons it describes reactions in terms of the movement of electrons.

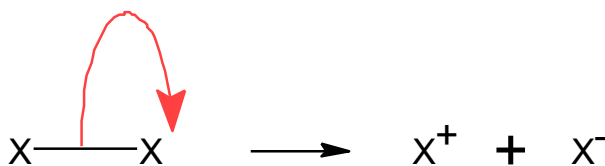
- **Definitions**

To help describe the mechanisms, first consider the meaning of these terms.

**Homolytic fission.** The breaking of a covalent bond in a symmetrical way, so that of the resulting species takes only *one* electron from the bond. The resultant species (that have unpaired electrons) are called free radicals, and are highly reactive. (**NOTE: a half-head on the arrow represents the movement of just ONE electron**).



**Heterolytic fission.** The breaking of a covalent bond in an unsymmetrical way, so that one of the resulting species takes *both* electrons from the bond. This results in the formation a negative species and a positive species. (**NOTE: a full-head on the arrow represents the movement of TWO electrons**).



**Addition.** The joining together of two reactants to form a single product.

**Substitution.** A reaction where one atom, or group of atoms, is replaced by another atom, or group of atoms.

**Rearrangement.** A reaction where the same atoms are present in the product as in the reactant, but are combined in a different physical arrangement.

**Elimination.** A reaction where two small groups are removed from reactants, in order to produce a main product and a by-product (the by-product is the combination of the removed groups).

**Electrophile.** A species that seeks out a negative area, and is capable of accepting a pair of electrons to form a covalent bond. It may have a positive charge or simply be electron deficient and therefore be able to act as a Lewis acid.

**Nucleophile.** A species that seeks out a positive area, and has a pair of electrons it can donate to form a covalent bond. It may have a negative charge or simply have a lone pair of electrons to donate and therefore be able to act as a Lewis base.



- **Hybridization**

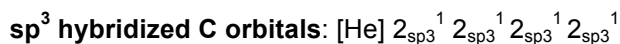
To understand some specific mechanisms in full, it is necessary to consider the hybridization of carbon.

### Alkanes & $sp^3$ hybridization

Consider the ground, and one potential excited state of the carbon atom. (The excited state is achieved by the input of energy).

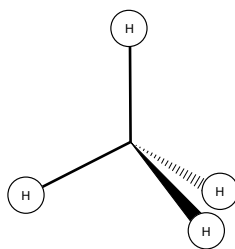


The excited state orbitals, rather than remaining as one s and three p orbitals, mix to produce four equivalent  $sp^3$  hybrid orbitals.



These hybrid orbitals arrange themselves in a tetrahedral shape around the carbon atom and can overlap with suitable half-filled orbitals on other atoms, forming  $\sigma$  bonds, e.g., with hydrogen atoms as in methane,  $\text{CH}_4$ .

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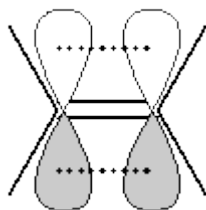
### Alkenes, benzene & $sp^2$ hybridization

Again, following the input of energy there can be a mixing of orbitals, this time producing three equivalent  $sp^2$  hybrids and *leaving one p orbital unhybridized*.



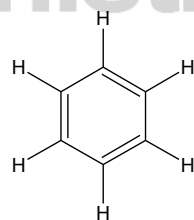
When two carbon atoms that are  $sp^2$  hybridized come together, one  $\sigma$  bond is formed between the carbon atoms and four  $\sigma$  bonds are formed between the carbon atoms and hydrogen atoms (two for each C).

Overlap of the *unhybridized* p orbital forms a  $\pi$  bond, thus creating the double bond ( $\sigma + \pi$ ) between the two carbon atoms. The consequence of the  $\pi$  bond is that above and below the C to C bond, there is a large area of negative charge making alkenes susceptible to *electrophilic* attack.

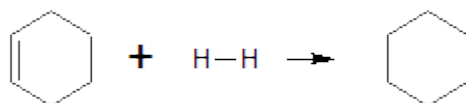


Any carbon atom that makes one double bond and two single sigma bonds will be  $sp^2$  hybridized. One consequence of  $sp^2$  hybridization, and the formation of C=C bonds, is that the geometry around the bond will be planar (flat).

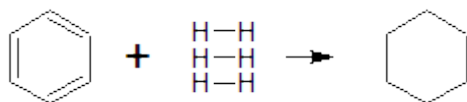
The Kekulé structure originally given for benzene ( $C_6H_6$ ) suggests a flat molecule with three, localized double bonds (bond order of 2), alternate with three single bonds (bond order of 1). This structure could not explain the fact that benzene is reluctant to undergo addition reactions with, for example, hydrogen, unless extreme conditions of temperature, pressure and catalysts are applied. If benzene were truly a simple cyclic alkene, then addition reactions would occur with ease.



Consider the thermochemical data associated with the hydrogenation of cyclohexene. The process shown below has an enthalpy change =  $-120 \text{ kJmol}^{-1}$ .

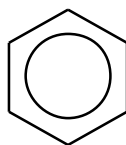


If benzene truly were a 'triene', when adding hydrogen across three of the carbon-carbon double bonds, we would expect an enthalpy change =  $(3) (-120 \text{ kJmol}^{-1}) = -360 \text{ kJmol}^{-1}$ . We actually find that the enthalpy change associated with the process below is closer to  $-208 \text{ kJmol}^{-1}$ .

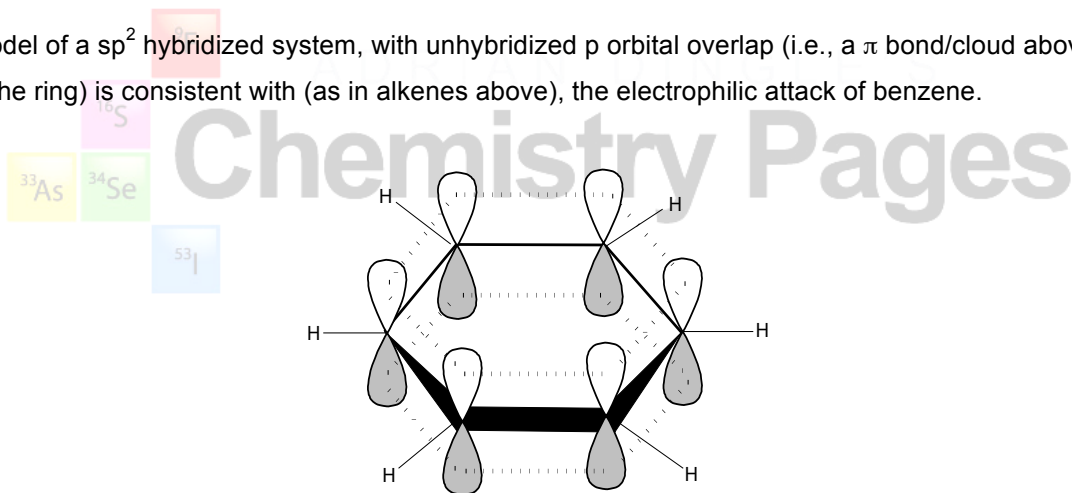


Also, X-ray studies suggest that the C–C bond lengths in benzene are all equivalent, and that they are intermediate in length between that of a single bond and double bond (bond order of 1.5). So, is there a better way to represent benzene than the single-double-single-double-single-double structure proposed by Kekulé?

In short yes, and it shows a delocalized electron system of pi electrons, rather than a localized system of alternate single and double bonds.

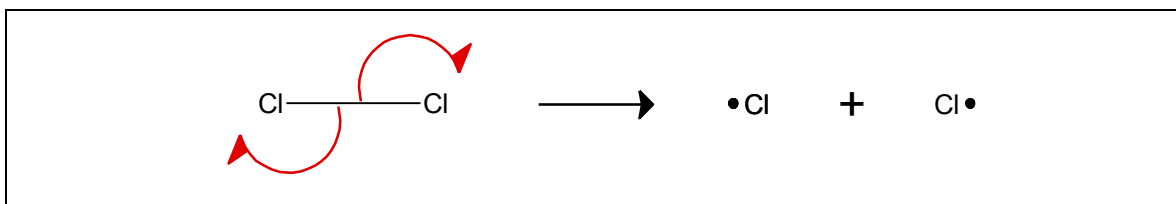


The model of a  $sp^2$  hybridized system, with unhybridized p orbital overlap (i.e., a  $\pi$  bond/cloud above and below the ring) is consistent with (as in alkenes above), the electrophilic attack of benzene.

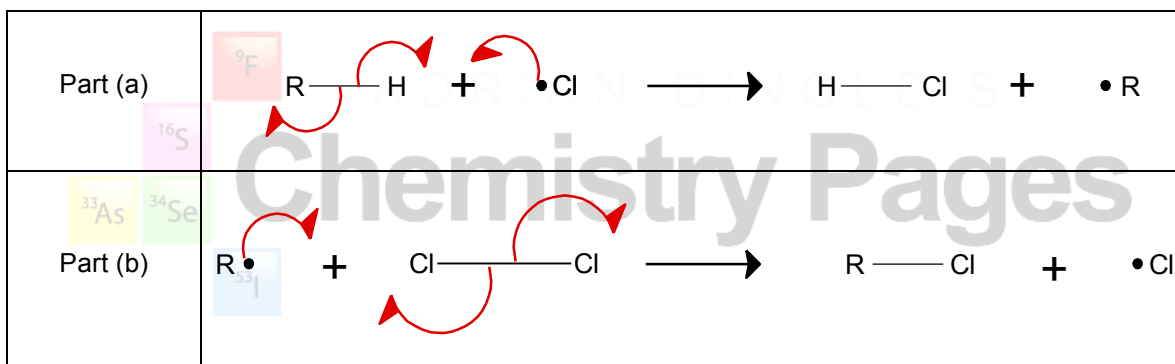


- **Homolytic, free radical, substitution. Alkanes with halogens.** e.g., methane with chlorine in the presence of ultra-violet light.

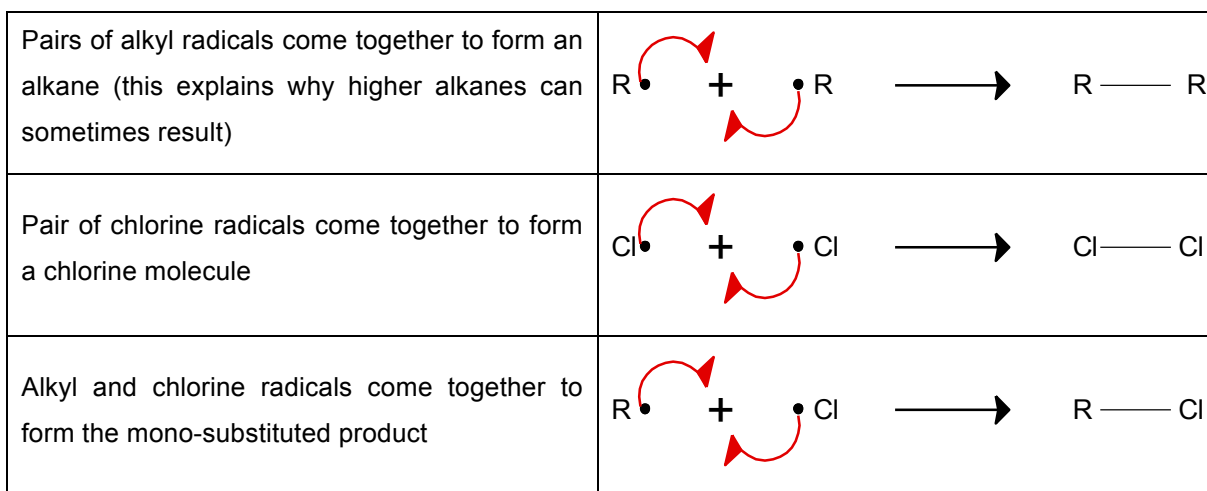
Initiation. Homolytic bond fission of chlorine initiated by ultra-violet light. Chlorine free radicals are produced. A free radical is a species with an unpaired electron and as such is extremely reactive.



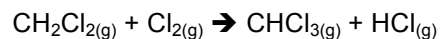
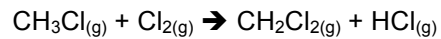
Propagation. The chlorine free radical removes H from methane (in this case R = CH<sub>3</sub>). The methyl radical formed in part (a) below, reacts with an undissociated chlorine molecule to produce chloromethane and a chlorine radical in part (b). This instigates a chain reaction, where the chlorine free-radical produced in part (b), goes back to being a reactant in part (a), and so on.



Termination. These steps produce no free radicals and lead to the termination of the reaction.



The substitution reaction can continue to yield further substituted products by the reaction of the monosubstituted product produced in part (b) of the propagation step, above, i.e., dichloro, trichloro and tetrachloro substitutions, each time a molecule of HCl being produced as a by-product.



etc.

Such a multi-product reaction has somewhat limited synthetic value due to the cost of separating the products and controlling the reaction. The reaction can be carried out using other alkanes and halogens.

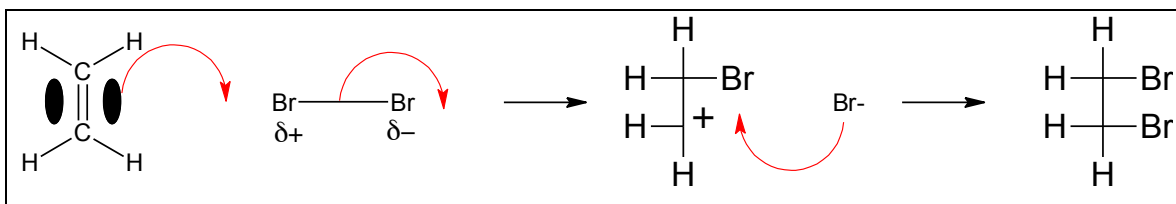




- **Heterolytic, electrophilic, addition.**

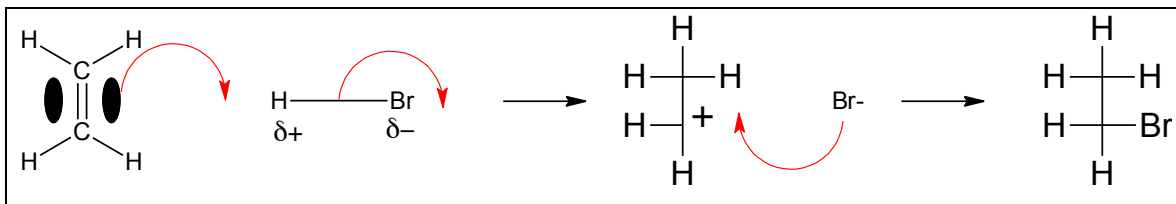
**(i) Alkenes with halogens.** e.g., ethene with bromine.

Consider the structure of double bond in ethene. Due to the  $\pi$  bond, caused by the overlap of unhybridized p orbitals, the alkene has a large area of negative charge around the double bond. This leads to the production of an induced dipole in the bromine molecule. The electron cloud around the double bond is attracted to the positive end of the bromine dipole causing the bromine bond to break heterolytically. This leads to the formation of a carbocation and a bromide ion. The final step involves the attack of the negative bromide ion on the carbocation. The product is 1,2-dibromoethane.



**(ii) Alkenes with hydrogen halides.** e.g., ethene with HBr.

A similar reaction mechanism is followed to that above but this time the hydrogen bromide molecule has a permanent dipole caused by a difference in electronegativity between H and Br and the product is bromoethane.

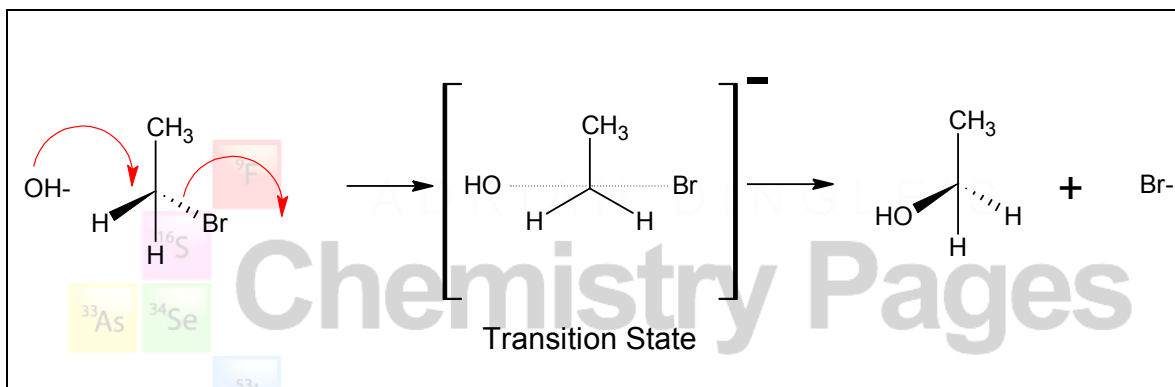


- Heterolytic, nucleophilic substitution.

(i) **Primary Halogenoalkanes with aqueous hydroxide ions.** e.g., bromoethane with aqueous NaOH.  
**S<sub>N</sub>2 mechanism.**

A primary halogenoalkane is one that has only one R (alkyl) group attached to the halogen bearing carbon.

The electronegative bromine atom causes a polarization of the C-Br bond, allowing the hydroxide ion to act as a nucleophile. The breaking of the C-Br bond and the formation of the O-C bond occur simultaneously leading to the formation of the transition state.

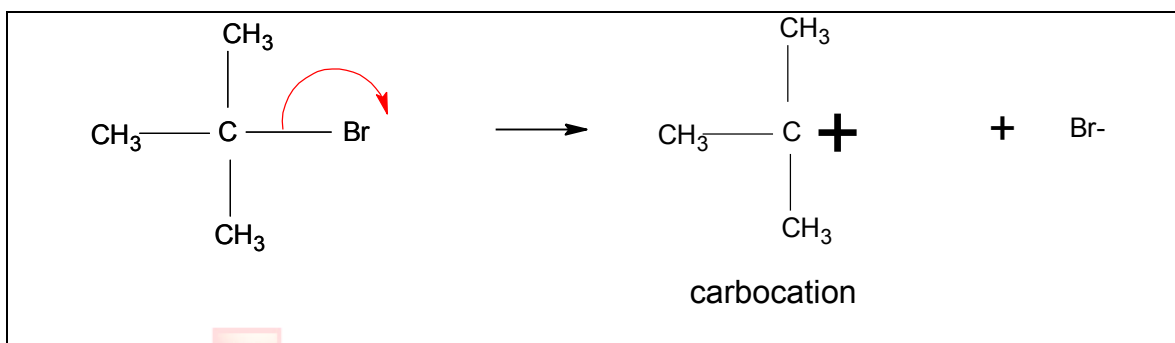


The rate is found to be 2<sup>nd</sup> order overall, i.e., dependent upon the concentration of the hydroxide ions and the halogenoalkane., i.e., rate = k[halogenoalkane][OH<sup>-</sup>].

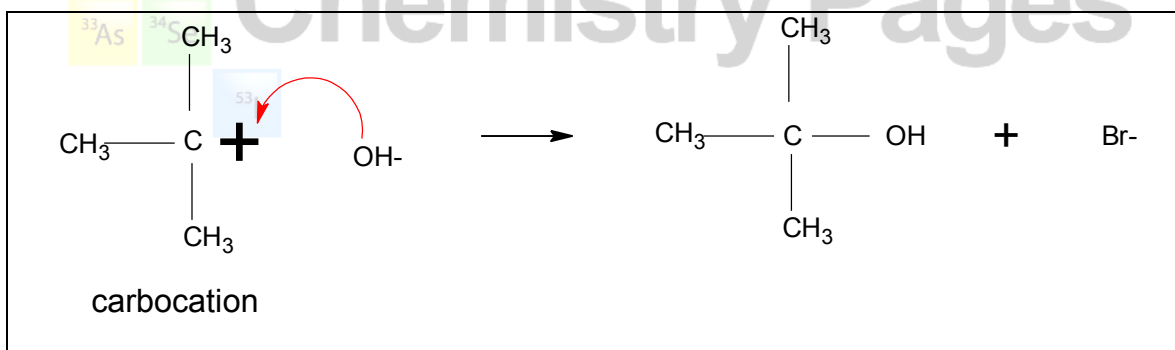
(ii) **Tertiary Halogenoalkanes with aqueous hydroxide ions.** e.g., 2-bromo-2-methylpropane with aqueous NaOH. **S<sub>N</sub>1 mechanism.**

A tertiary halogenoalkane is one that has three R (alkyl) groups attached to the halogen bearing carbon.

Again the electronegativity of the bromine atom plays a part, this time causing the complete fission of the C-Br bond to yield a carbocation.

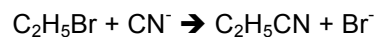


The hydroxide ions then act as nucleophiles to complete the reaction.



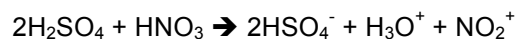
Here the first step is rate determining and only depends on the concentration of the haloalkane. It is first order overall, i.e., rate = k[halogenoalkane].

Similar reaction mechanisms occur with CN<sup>-</sup> ions acting as a nucleophile to yield a nitrile. These are extremely important reactions as they add to the length of the carbon chain. e.g.,

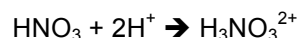


- **Heterolytic, electrophilic substitution.** e.g., reaction of benzene with mixed concentrated acids. ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ).

The electrophile in this reaction is  $\text{NO}_2^+$ , which is formed by the reaction between the two acids.



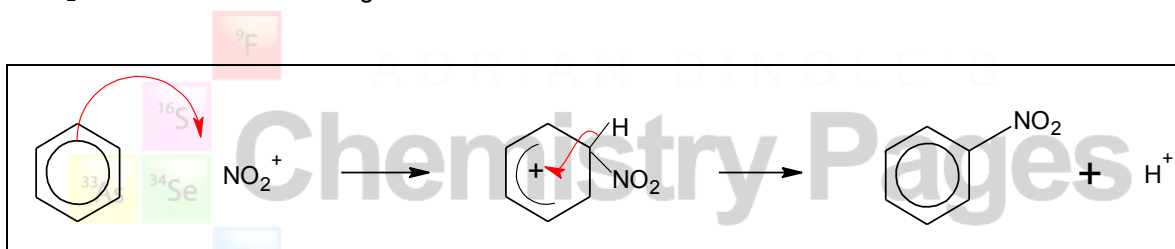
In this reaction the nitric acid acts as a base by accepting protons from the sulfuric acid.



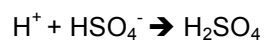
This species then breaks down to form the electrophile ( $\text{NO}_2^+$ ) and the hydronium ion.



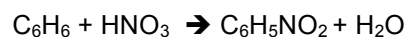
The  $\text{NO}_2^+$  ion then reacts according to the mechanism below.



The  $\text{H}^+$  ion produced will react with the  $\text{HSO}_4^-$  ion to regenerate sulfuric acid. The acid essentially acts as a catalyst.

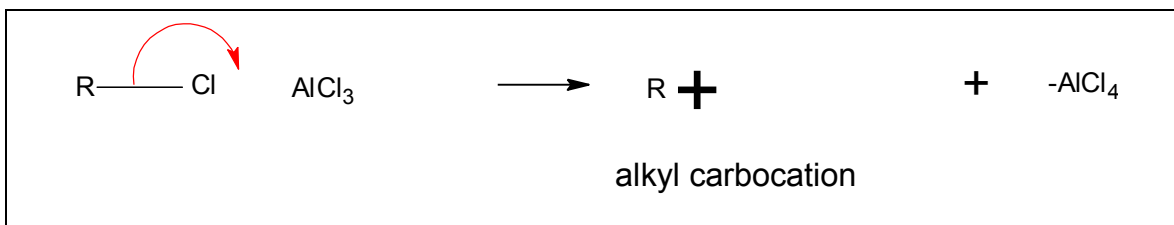


Overall the reaction can be considered to be

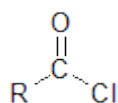


with the sulfuric acid omitted since it is a catalyst and as such, it ultimately remains unchanged.

Other electrophiles can be generated, and as a result other groups can be substituted on to the benzene ring. Most common are acylation and alkylation of the ring. In these reactions electron deficient  $\text{AlCl}_3$  is used as a catalyst to generate a carbocation (or carbonium ion) that can act as an electrophile thus;



An acyl carbocation can be generated in the same way using a carbonyl compound rather than R-Cl as the reagent.



The mechanism for the attack of the benzene ring with both of these nucleophiles is as with NO<sub>2</sub><sup>+</sup> above, this time HCl as the by-product, and the AlCl<sub>3</sub> catalyst is regenerated.

