Chem Factsheet

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Halogenation in Organic Chemistry

Halogenation is a chemical reaction that introduces one or more halogen atoms into a molecule. Halogenation can be subdivided into fluorination, chlorination, bromination, and iodination depending on which type of halogen atom is introduced.

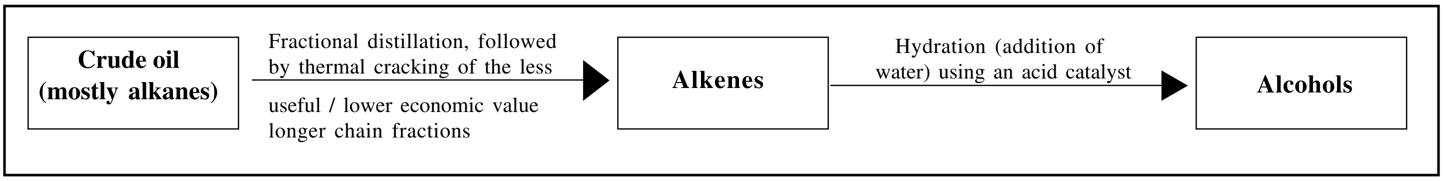
The importance of halogenation cannot be overstated. Many halogen compounds have commercial uses and, it is by introduction of a halogen atom in to a molecule that a variety of other functional groups can be obtained; i.e. halogenation is an important step in many organic syntheses.

When studying this FactSheet, since 'A' level specifications vary, refer to your particular specification to see whether each section is relevant or not.

A. Halogenoalkanes (Haloalkanes)

1. The Formation of Halogenoalkanes

Halogenoalkanes can be made from alkanes, alkenes and alcohols. However alcohols are usually made from alkenes and alkenes from alkanes, as summarised:



(a) From Alkanes

Alkanes can be chlorinated and brominated using the appropriate halogen at room temperature in the presence of UV light.
Methane and chlorine, for example, initially produce the gas chloromethane: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Free Radical Substitution Mechanism for methane reacting with chlorine to produce chloromethane

Step 1. Initiation: $Cl_2 \rightarrow 2Cl\bullet$

(UV light provides the energy for homolytic fission of the Cl_2 bond to form Cl free radicals)

Step 2. Propagation:
(i) $CH_4 + Cl\bullet \rightarrow HCl + \bullet CH_3$ and
(ii) $Cl_2 + \bullet CH_3 \rightarrow CH_3Cl + Cl\bullet$

(The formation of Cl• in propagation step (ii) means propagation step (i) will continue as long as methane is still present.)

Step 3.Termination:
e.g. $2\bullet CH_3 \rightarrow C_2H_6$

The combination of two free radicals stops propagation continuing.

A disadvantage with this method is that further substitution can occur leading to the formation of di-, tri- and tetrachloromethane mixed with chloromethane. These liquids can be separated by fractional distillation but this involves an extra cost. A higher molar ratio of methane to chlorine will produce a higher proportion of chloromethane whereas an excess of chlorine will increase the yield of tetrachloromethane.

(b) From Alkenes

(i) The Introduction of One Halogen Atom Using Hydrogen Halides

- Symmetrical alkenes produce a single addition product.
  e.g. Only 2-bromo-2,3-dimethylbutane is formed when 2,3-dimethylbut-2-ene reacts with HBr(g).

$$(CH_3)_2C{=}C(CH_3)_2 + HBr \rightarrow (CH_3)_2CHCBr(CH_3)_2$$

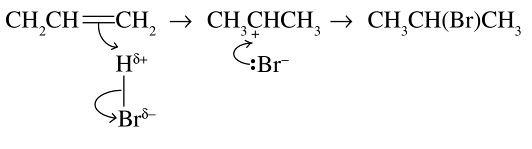
- Unsymmetrical alkenes produce two addition products.
  e.g. Propene reacts with HBr to produce both 2-bromopropane (≈ 90%) and 1-bromopropane (≈ 10%)

These reactions follow an ***electrophilic addition mechanism*** which has two steps:

Step 1: is the rate determining step. The two pi electrons of the alkene double bond form a dative bond with the proton produced when the polar HBr bond undergoes heterolytic fission .

Step 2: is the rapid reaction of the negative bromide ion (a nucleophile) with the carbocation.

Electrophilic Addition Mechanism of HBr to Propene to Produce 2-Bromopropane



Two products are possible with unsymmetrical alkenes because in step1 a primary or a secondary carbocation can be formed. The mechanism shows the formation of the more stable secondary carbocation. Hence there is a greater yield of the 2-bromopropane isomer.

Stability of Alkyl Carbocations: **tertiary > secondary > primary**. The greater the number of electron donating alkyl groups (tert 3 > sec 2 > prim 1) attached to the positively-charged carbon atom, the more the positive charge will be spread over the whole ion and the more stable the carbocation will be.

(ii) The Introduction of Two Halogen Atoms using Halogens (not fluorine).

Alkenes react with the halogens chlorine, bromine and iodine, either as the element or in an organic solvent to produce dihalogenoalkanes.

e.g. Propene reacts with bromine to form 1,2-dibromopropane.

$$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br.$$

The mechanism is analogous to the electrophilic addition of a hydrogen halide.

With bromine:

Step 1: the two pi electrons of the alkene double bond form a dative bond with Br^+ produced when the polarised bromine molecules undergoes heterolytic fission. (The bromine molecule is polarised $Br^{\delta+}$ —$Br^{\delta-}$ as it approaches the pi electron cloud of the double bond.)

Step 2: occurs as with hydrogen bromide.

Note If water is the solvent for bromine then the water molecule becomes the main nucleophile in step 2. Hence, 1-bromopropan-2-ol is the main product derived from the more stable secondary carbocation.

The equation is:

$$CH_3CH{=}CH_2 + Br_2 + H_2O \rightarrow CH_3CH(OH)CH_2Br + HBr$$

Note The rapid decolouration of an orange-brown bromine solution is a test for a C=C group.

(c) From alcohols

The substitution of the –OH group of an alcohol by a halogen atom can be achieved in various ways. The method chosen depends on the halogen to be introduced.

(i) Fluoro- and Chloroalkanes

The alcohol is refluxed with a mixture of a group I halide (e.g. KF or KCl) and concentrated sulfuric acid.

The metal halide and acid react to produce the hydrogen halide *in situ* which then reacts with the alcohol.

e.g. $KCl + H_2SO_4 \rightarrow HCl + KHSO_4$
followed by: $CH_3CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2Cl + H_2O$

This method is unsuitable for preparing bromo- and iodoalkanes since HBr and HI are sufficiently strong reducing agents to reduce the concentrated sulfuric acid. HBr reduces the acid to SO_2 and HI reduces the acid eventually to H_2S as it is a stronger reductant than HBr. In other words, the acid oxidises the HBr and HI to Br_2 and I_2 respectively.

(ii) Bromo- and Iodoalkanes

The alcohol is heated with a mixture of red phosphorus and the halogen. PBr_3 / PI_3 is initially formed which then reacts with the alcohol.

e.g. $P + 1\frac{1}{2}I_2 \rightarrow PI_3$
followed by: $3CH_3CH_2CH_2OH + PI_3 \rightarrow 3CH_3CH_2CH_2I + H_3PO_3$

(iii) Chloroalkanes

The alcohol is mixed with phosphorus(V) chloride at room temperature. (This is essentially is the same as ii) but the phosphorus halide is used directly.)

e.g. $CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + HCl + POCl_3$

Note: This is also used as a test for an –OH group as steamy fumes of hydrogen chloride are produced. Water, carboxylic acids and alcohols all have –OH groups and hence, all produce steamy fumes.

B. Acyl Chlorides

1. The formation of acyl chlorides

This is analogous to (c) (iii). A carboxylic acid is chlorinated using phosphorus (V) chloride

e.g. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + PCl_3O$

C. Halogenobenzenes

1. The formation of halogenobenzenes

Electrophilic substitution occurs with chlorine or bromine in the presence of a halogen carrier – i.e. a Friedel-Crafts catalyst.

e.g. Bromination of benzene occurs with bromine in the presence of $FeBr_3$

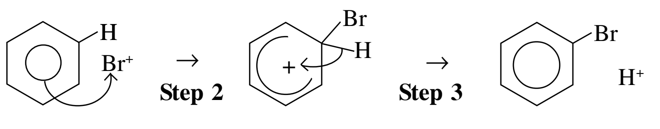
$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

Electrophilic Substitution Mechanism for the Monobromination of Benzene

Step 1: formation of the Br^+ electrophile:
$Br_2 + FeBr_3 \rightarrow Br^+ + [FeBr_4]^-$

Step 2: the electrophile accepts two of the six delocalised pi electrons producing an intermediate.

Step 1: Formation of the Br^+ electrophile: $Br_2 + FeBr_3 \rightarrow Br^+ + [FeBr_4]^-$

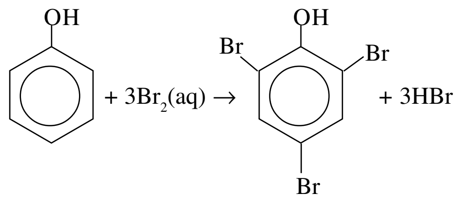


Step 4: The catalyst is reformed: $H^+ + [FeBr_4]^- \rightarrow FeBr_3 + HBr$

Step 3: full delocalisation is restored as a proton is released.

Step 4: reforming the catalyst $H^+ + [FeBr_4^-] \rightarrow HBr + FeBr_3$.

Note Phenol (C_6H_5OH) reacts with bromine water (an orange-brown solution) at room temperature to form a white precipitate of 2,4,6-tribromophenol. No halogen carrier / $FeBr_3$ catalyst is needed.



A lone pair of p electrons on the O atom is partially delocalised into the ring causing its electron density to increase relative to that in benzene.Thus electrophiles are more readily attracted and the rate of the bromination is faster.

Practice Questions

1. (a) Write balanced equations using structural formula for the formation of 1-chlorobutane from
   (i) butane and chlorine,
   (ii) but-1-ene and hydrogen chloride,
   (iii) butan-1-ol, KCl and conc. H_2SO_4. State the types of reactions occurring.

   (b) Explain why methods (i) and (ii) are likely to produce lower yields of 1-chlorobutane than method (iii).

2. Naturally occurring carboxylic acids usually have an even number of carbon atoms per molecule of acid. How can $CH_3(CH_2)_7COOH$ be made from $CH_3(CH_2)_6COOH$. Answer by writing equations for each step, the reagents needed and the types of the reaction occurring.

   The first step is a reduction using $LiAlH_4$. $CH_3(CH_2)_6COOH + 4[H] \rightarrow CH_3(CH_2)_6CH_2OH$

3. Chlorofluorcarbons (CFC's) such as $CF_2ClCFCl_2$ that were used as coolants in refrigerators have been replaced by hydrochlorofluorcarbons (HCFC's) such as $CHClF_2$ as these break down at lower altitudes.
   Draw a skeletal formula of $CHF_2CHClBr$ and give its IUPAC name. Briefly explain why it is important they break down at lower altitudes.

4. Complete the reaction sequence for the conversion of ethene into1,4-diaminobutane by drawing the structure of compounds A and B. State the reagents and conditions for each step and write the mechanism for Step 1.

   $$H_2C{=}CH_2 \xrightarrow{\text{Step 1}} \text{Compound A} \xrightarrow{\text{Step 2}} \text{Compound B} \xrightarrow{\text{Step 3}} H_2NCH_2CH_2CH_2CH_2NH_2$$

5. (a) What is the major product formed when methyl benzene reacts with excess chlorine in UV light?
   (b) What reagent and essential condition is needed to convert methyl benzene into a mixture containing 1-chloro-4-methylbenzene?
   In (a) and (b) what type of mechanism is occurring and identify one other product that could be produced.

Answers

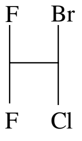
1. (a) (i) $CH_3CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2CH_2Cl + HCl$. Substitution
   (ii) $CH_3CH_2CH{=}CH_2 + HCl \rightarrow CH_3CH_2CH_2CH_2Cl$. Addition
   (iii) $CH_3CH_2CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2CH_2Cl + H_2O$
   Substitution ($KCl + H_2SO_4 \rightarrow HCl + KHSO_4$)

   (b) Method (i) will also produce 2-chlorobutane and further substitution since other H atoms are available.
   Method (ii) will produce mainly 2-chlorobutane as the secondary carbocation $CH_3CH_2C^+HCH_3$ is more stable than the primary carbocation, $CH_3CH_2CH_2C^+H_2$
   In Method (iii) $CH_3CH_2CH_2CH_2Cl$ is the only substitution product possible.

2. Step 2: e.g. $CH_3(CH_2)_6CH_2OH + HCl \rightarrow CH_3(CH_2)_6CH_2Cl + H_2O$.
   KCl and conc. H_2SO_4. Substitution.

   Step 3: $CH_3(CH_2)_6CH_2Cl + KCN \rightarrow CH_3(CH_2)_6CH_2CN$.
   KCN in ethanol. Substitution.

   Step 4: $CH_3(CH_2)_6CH_2CN + HCl + 2H_2O \rightarrow CH_3(CH_2)_6CH_2COOH + NH_4Cl$.
   HCl(aq). Hydrolysis.

3. 

   1-bromo-1-chloro-2,2-difluoroethane.
   When CFCs break down they produce chlorine free radicals. If they are produced in the upper atmosphere they catalyse the breakdown of ozone, thus destroying the ozone layer that protects the earth from harmful UV.

4. A is $CH_2(Br)CH_2Br$ Step 1: pass ethene gas in to bromine at room temperature.
   B is $CH_2(CN)CH_2CN$
   Step 2: reflux with excess KCN in ethanol.
   Step 3: H_2 / Ni or $LiAlH_4$
   Mechanism. See page 1

5. (a) $C_6H_5CCl_3$.
   (b) $Cl_2(g)$ and $AlCl_3$.
   (c) Free radical substitution, electrophilic substitution. e.g. $C_6H_5CHCl_2$, e.g. 1-chloro-2-methylbenzene.

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