

Properties of Alkyl Halides.

(1) Physical properties

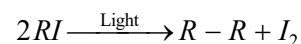
(i) CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl are gases at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.



(vi) For a given alkyl group, the boiling points of alkyl halides are in the order

$RI > RBr > RCl > RF$ and for a given halogen the boiling points of alkyl halides increase with the increase of the size of the alkyl group.

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

(2) Chemical properties: The alkyl halides are highly reactive, the order of reactivity is,

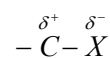
Iodide > Bromide > Chloride (Nature of the halogen atom)

Tertiary > Secondary > Primary (Type of the halogen atom)

Amongst the primary alkyl halide, the order of reactivity is : $CH_3X > C_2H_5X > C_3H_7X$, etc.

The high reactivity of alkyl halides can be explained in terms of the nature of $C-X$ bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms.

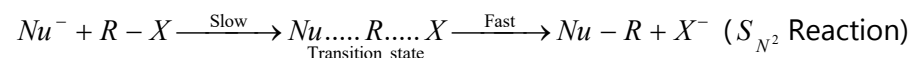
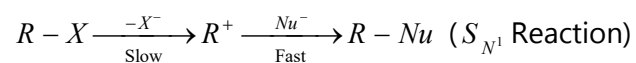
The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, i.e., halogen acquires a small negative charge and carbon a small positive charge.



This polarity gives rise to two types of reactions,

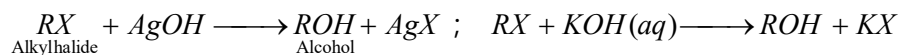
(i) Nucleophilic substitution reactions (ii) Elimination reactions

(i) Nucleophilic substitution reactions: The $C^{\delta+}$ site is susceptible to attack by nucleophiles (An electron rich species). $:Nu^- + R-X \longrightarrow Nu-R + X^-$:

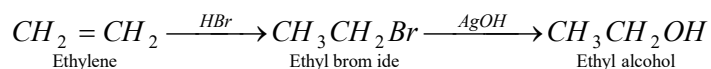


Examples of S_N reactions,

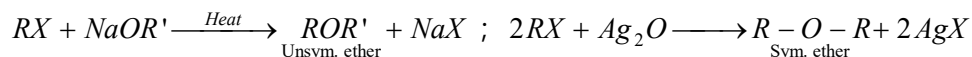
(a) Hydrolysis: Alkyl halides are hydrolyzed to corresponding alcohols by moist silver oxide (*AgOH*) or by boiling with aqueous alkali solution (*NaOH* or *KOH*). The attacking nucleophile is *OH*⁻.



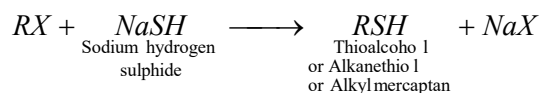
Note: With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with *HBr* to form alkyl bromide and then hydrolysis is done.



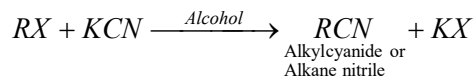
(b) Reaction with alkoxides or dry silver oxide: Ethers are formed by heating alkyl halides with sodium or potassium alkoxides or dry silver oxide. The attacking nucleophile is *OR*⁻ (Williamson's synthesis).



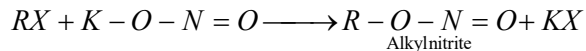
(c) Reaction with sodium or potassium hydrogen sulphide: Alkyl halides form thioalcohols with aqueous alcoholic sodium hydrogen sulphide or potassium hydrogen sulphide. The nucleophile is *SH*⁻.



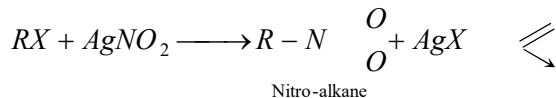
(d) Reaction with alcoholic potassium cyanide and silver cyanide: Alkyl cyanides are formed as the main product when alkyl halides are heated with alcoholic potassium cyanide. The nucleophile is *CN*⁻.



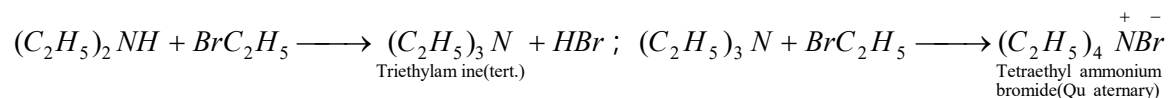
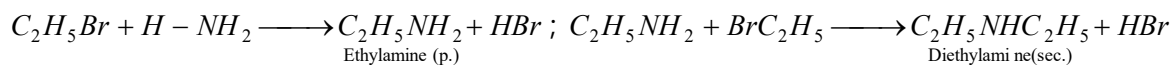
(e) Reaction with potassium nitrite or silver nitrite: On heating an alkyl halide with potassium nitrite in an aqueous ethanolic solution, alkyl nitrite is obtained as the main product though some nitro alkane is also formed. The nucleophile is *NO*₂⁻.



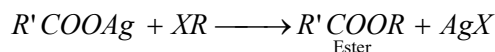
However, when alkyl halide is heated with silver nitrite in an aqueous ethanolic solution, nitroalkane is the main product. Some alkyl nitrite is also obtained.



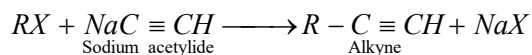
(f) Reaction with ammonia: On heating with aqueous or alcoholic solution of ammonia in a sealed tube at 100°C, alkyl halides yield a mixture of amines and quaternary ammonium salt. The nucleophile is NH_2^- in the first reaction.



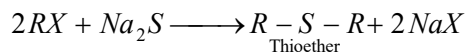
(g) Reaction with silver salts of fatty acids: On heating with silver salts of fatty acids in alcoholic solution, alkyl halides yield esters. The nucleophile is $R'COO^-$.



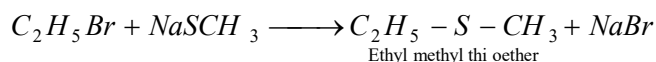
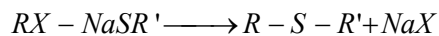
(h) Reaction with sodium acetylide: Alkyl halides react with sodium acetylide to form higher alkynes. The nucleophile is $CH \equiv C^-$.



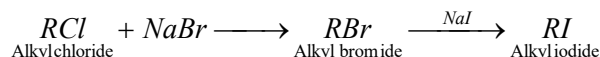
(i) Reaction with sodium or potassium sulphide: Alkyl halides react with sodium or potassium sulphide in alcoholic solution to form thioethers.



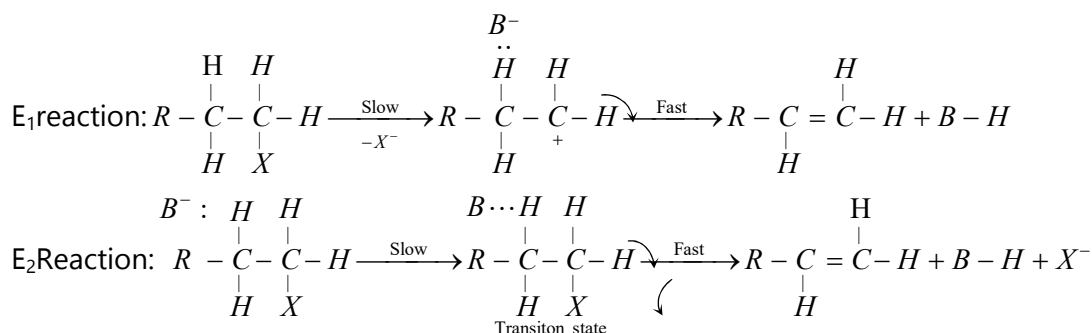
Thioethers can also be obtained by heating alkyl halides with alcoholic solution of sodium mecaptide ($NaSR'$), i.e., metallic derivative of a thioalcohol.



(j) Reaction with halides: Alkyl chlorides react with sodium bromide or sodium iodide to form alkyl bromide or alkyl iodide. Similarly, alkyl bromides react with sodium iodide in acetone or methanol to form alkyl iodides.



(ii) Elimination reactions: The positive charge on carbon is propagated to the neighboring carbon atoms by inductive effect. When approached by a strongest base (B), it tends to lose a proton usually from the β -carbon atom. Such reactions are termed elimination reactions. They are also E_1 and E_2 reactions.

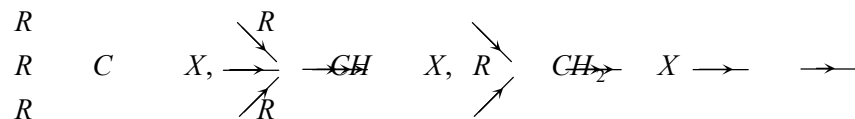


As the above reactions involve leaving of X^- , the reactivity of alkyl halides (Same alkyl group, different halogens) should be limited with $C-X$ bond strength.

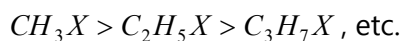
Type of bond	$C-I$	$C-Br$	$C-Cl$
Bond strength (kcal/mol)	45.5	54	66.5

$\xrightarrow{\hspace{10em}}$
 Bond strength increases

The breaking of the bond becomes more and more difficult and thus, the reactivity decrease. The order of reactivity (Tertiary > Secondary > Primary) is due to +I effect of the alkyl groups which increases the polarity of $C-X$ bond.

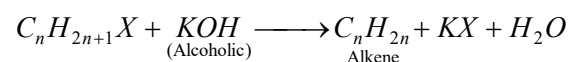


The primary alkyl halides undergo reactions either by S_N2 or E_2 mechanisms which involve the formation of transition state. The bulky groups cause steric hinderance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues.

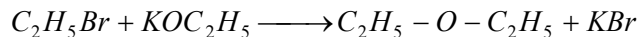


Example of elimination reaction

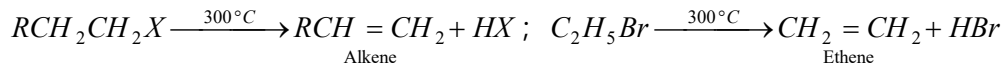
(a) Dehydrohalogenation: When alkyl halides are boiled with alcoholic potassium hydroxide, alkenes are formed.



In this reactions, ether is a by-product as potassium ethoxide is always present in small quantity.



(b) Action of heat: Alkyl halides when heated above 300°C, tend to lose a molecule of hydrogen halide forming alkenes.



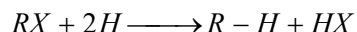
The decomposition follows the following order,

Iodide > Bromide > Chloride (When same alkyl group is present) and

Tertiary > Secondary > Primary (When same halogen is present).

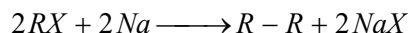
(iii) Miscellaneous reactions

(a) Reduction: Alkanes are formed when alkyl halides are reduced with nascent hydrogen obtained by Zn/HCl or sodium and alcohol or Zn/Cu couple or $LiAlH_4$.

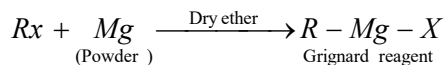


Reaction is used for the preparation of pure alkanes

(b) Wurtz reaction: An ether solution of an alkyl halide (Preferably bromide or iodide) gives an alkane when heated with metallic sodium.



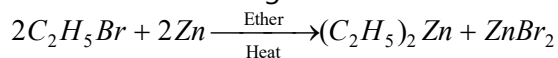
(c) Reaction with magnesium: Alkyl halides form Grignard reagent when treated with dry magnesium powder in dry ether.



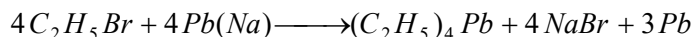
Grignard reagents are used for making a very large number of organic compounds.

(d) Reaction with other metals: Organometallic compounds are formed.

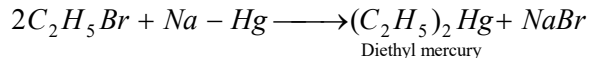
☐ When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called Frankland reagents.



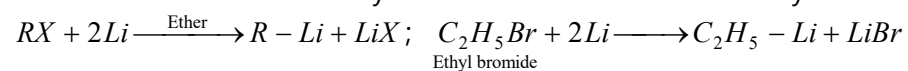
☐ When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead which is used as an antiknock compound in petrol.



☐ Alkyl halides form dialkyl mercury compounds when treated with sodium amalgam.

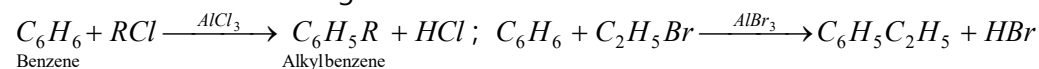


□ Reaction with lithium: Alkyl halides react with lithium in dry ether to form alkyl lithiums.



Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also.

(e) Friedel-Craft's reaction: Alkyl halides react with benzene in presence of anhydrous aluminium halides to form a homologue of benzene.



(f) Substitution (Halogenation): Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.

