Identification of Alkyl and Aryl Halides

Physical properties

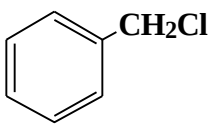
All alkyl halides and chlorobenzene are colourless liquids when pure except iodoform, CHI_3, which is a yellow crystalline solid with a characteristic odour. Methyl iodide, ethyl iodide and bromide, chloroform, and carbon tetrachloride have sweetish odours. Benzyl chloride has a sharp irritating odour and is lachrymatory. Chlorobenzene possesses aromatic odour.

Alkyl and aryl halides (R–X, Ar–X) have boiling points higher than the parent hydrocarbon because of the heavier molecular weight. Accordingly, for a given compound, iodides have the higher boiling point than bromides and chlorides.

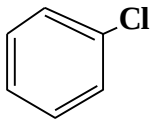
In spite of their polarity alkyl halides are insoluble in water due to their inability to form hydrogen bonds. They are soluble in most organic solvents.

Iodo-, bromo-, and polychloro- compounds are denser than water.

CH_3X	C_2H_5-X	$CHCl_3$	CCl_4
metheyl halide	ethyl halide	chloroform	carbon tetrachloride



benzyl chloride

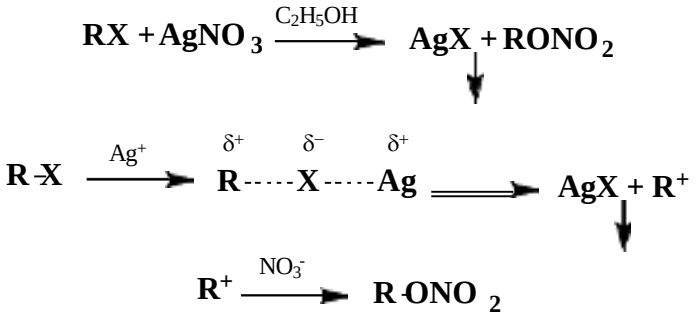


chlorobenzene

Chemical reactions

1. Reaction with alcoholic silver nitrate.

Alcoholic silver nitrate reagent is useful in classifying halogen compounds. Many halogen containing compounds react with silver nitrate to give an insoluble silver halide (AgX), and the rate of this reaction indicates the degree of reactivity of the halogen atom in the compound. Besides, the identity of the halogen can sometimes be determined from the colour of the silver halide produced; silver chloride is white (turns to purple on exposure to light), silver bromide is pale yellow, and silver iodide is yellow. These should, of course, be consistent with results from elemental analysis (sodium fusion for detection of halogens).



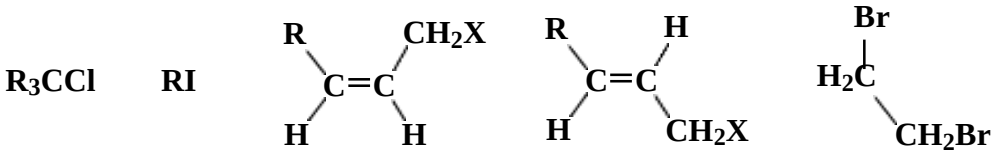
It is obvious that this reaction follows S_N1 mechanism. Generally the reactivity of alkyl halides towards this reagent is:

$$R_3CX > R_2CHX > RCH_2X$$

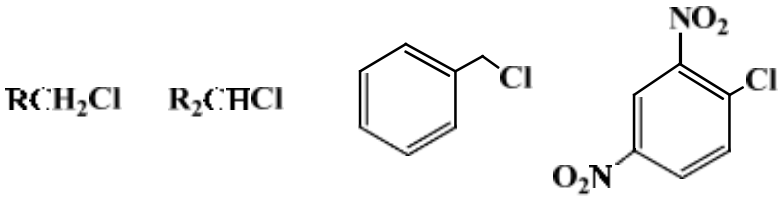
Procedure

Add one drop or a couple of crystals of the unknown to 2 mL of 2% ethanolic silver nitrate solution. If no immediate reaction is observed, stand for 5 minutes at room temperature and observe the result. If no reaction takes place, warm the mixture in water bath for 30 seconds and observe any change. If there is any precipitate (AgX) add several drops of 1 *M* nitric acid solution to it; silver halides are insoluble in this acid.

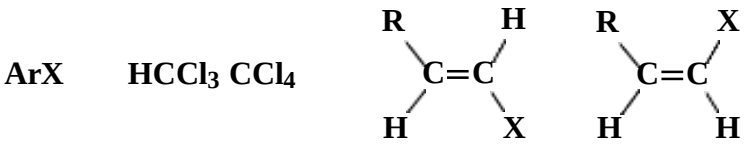
tert- chlorides, methyl and ethyl iodides, allylic chlorides, and ethyl bromides give fast result at room temperature:



pri- and *sec*- chlorides, benzyl chloride, and 1-chloro-2,4-dinitrobenzene give result only on warming:



Chlorobenzene, chloroform, iodoform, carbon tetrachloride, and vinylic chlorides don't give any positive result even on heating:



Cyclohexyl halides exhibit a decreased reactivity when compared with the corresponding open-chain secondary halides. Cyclohexyl chloride is inactive, and cyclohexyl bromide is less reactive than 2-

bromohexane, although it will give a precipitate with' alcoholic silver nitrate.

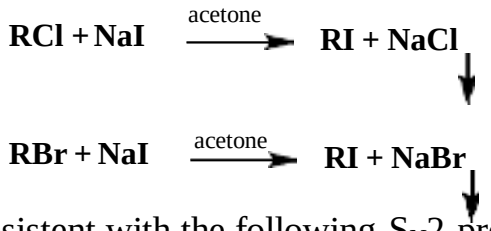
2. Sodium iodide in acetone test.

This test, complementing the alcoholic silver nitrate test, is used to classify aliphatic chlorides and bromides as primary, secondary, or tertiary. This test depends on the fact that sodium chloride and sodium bromide are only very slightly soluble in acetone.

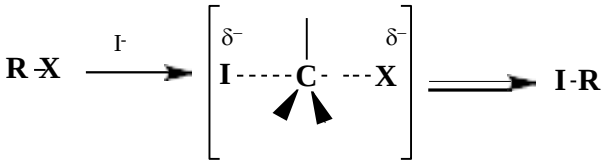
The mechanism follows direct displacement (S_N2) process; therefore, the order of reactivity of simple halides is:

primary> secondary> tertiary

With sodium iodide, primary bromides give a precipitate of sodium bromide within 3 min at 25°C, whereas the chlorides give no precipitate and must be heated to 50°C in order to effect a reaction. Secondary and tertiary bromides react at 50°C, but the tertiary chlorides fail to react within the time specified. Tertiary chlorides will react if the test solutions are allowed to stand for a day or two.



These results are consistent with the following S_N2 process:



Procedure

To 1 mL of the sodium iodide-acetone reagent in a test tube add two drops of the compound. If the compound is a solid, dissolve about 0.1 g in the smallest possible volume of acetone, and add the solution to the reagent. Shake the test tube, and allow the solution to stand at room temperature for 3 min. Note whether a precipitate is formed and also whether the solution turns reddish brown, because of the liberation of free iodine. If no change occurs at room temperature, place the test tube in water bath at 50°C.Excessive heating causes loss of acetone and precipitation of sodium iodide, which can lead to false-positive results. At the end of 6 min, cool to room temperature and note whether a reaction has occurred. Occasionally, a precipitate forms immediately after combination of the reagents; this represents a positive test only if the

precipitate remains after the mixture is shaken and allowed to stand for 3 minutes.

3. Differentiation between alkyl and aryl halides (Formaldehyde- sulfuric acid test)

With this test aryl halides (chlorobenzene) produce pink, red, or bluish red colour whereas alkyl halides produce yellow, amber, or brown colour.

Procedure

This reagent is prepared at the time of use by adding 1 drop of formaldehyde to a test tube containing 1 mL concentrated sulfuric acid. In another test tube add 1 drop of the compound to be tested to 1 mL of hexane. From this solution take 1-2 drops and add them to 1 mL of the reagent. Shake well and observe the colour.

4. Special tests for chloroform

a) Riemer- Tiemann reaction

For procedure and chemical equations refer to "Identification of Phenols" experiment. Resorcinol results in a red colour with slight fluorescence in the aqueous layer while α- or β- naphthol results in a deep blue aqueous layer fading to green.

b) Reduction of Fehling's reagent

For preparation of Fehling's reagent and chemical equations refer to "Identification of Aldehydes and Ketones" experiment. Boil 1 mL of chloroform gently (water bath) with 3 mL of Fehling's reagent with constant shaking for 3- 4 minutes. Reduction occurs and reddish cuprous oxide slightly separates.