Beckfoot

Subject: Chemistry	Topic: Halogenoalkanes 3.3.3	Year Group: 12

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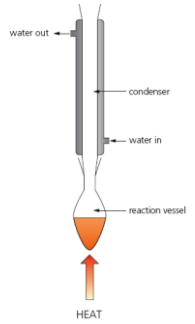
Properties of halogenoalkanes

1	Halogenoalkanes contain at least one C-X bond, where X is a halogen atom. The bond is polar due to the relatively high electronegativity of the halogen compared to the carbon atom. As fluorine is the most electronegative element, the C-F bond is the most polar bond, followed by C-Cl, C-Br and finally C-I.
2	The boiling point of the halogenoalkanes increases moving down the group i.e. CH_3I has a higher boiling point than CH_3Cl. This is due to the increased strength of the van der Waals' forces in CH_3I, since iodine is a bigger atom, and therefore has more electrons than chlorine.

Reacting halogenoalkanes

1	Due to the volatility of the halogenoalkanes, in order to heat them in a reaction they must be heated under reflux. In this process, the organic compound will be in a cycle of evaporating and condensing. This ensures that the particles are hot enough to react, without having them evaporate and escape in to the surroundings.



CFCs and the Ozone layer

1	CFCs (ChloroFluoroCarbons) are halogenoalkanes used as refrigerants, in aerosols and as solvents, and were popular due to the fact they were inert and non-toxic. In the upper layers of the atmosphere, the C-Cl bond (which is weaker than a C-F bond) is broken by UV light in homolytic fission.
2	
3	The chlorine radical that forms can then react with ozone, a gas that absorbs potentially harmful UV rays from reaching the earth, which may cause skin cancer, cataracts and damage to plant life. The equation for the breakdown of ozone by chlorine radicals is: $O_3 + Cl\bullet \rightarrow ClO\bullet + O_2$ $O_3 + ClO\bullet \rightarrow Cl\bullet + 2O_2$ Note that the $Cl\bullet$ is regenerated at the end, showing that it is a catalyst. The overall equation is $2O_3 \rightarrow 3O_2$, and a single chlorine radical can destroy 100000 O_3 molecules.
4	HFCs (HydroFluoroCarbons) have been synthesised to replace CFCs, as no $Cl\bullet$ are formed, and so do not destroy O_3.

Key Vocabulary

1	Substitution	A reaction whereby one atom or group of atoms is replaced by another atom or group of atoms.
2	Nucleophile	An electron pair donor.
3	Homolytic Fission	The breaking of a covalent bond where each atom gains one of the electrons from the pair.
4	Ozone	A gas with the formula O3 that is found in the upper atmosphere.
5	Free Radical	A species containing an unpaired electron.
6	Reflux	The continuous boiling and condensing of a mixture.
7	Hydrolysis	The breaking of chemical bonds with water.
8	Elimination Reaction	A reaction in which a small molecule is removed from the organic compound.
9	Base	Proton acceptor.

Reacting halogenoalkanes with NaOH

1	Halogenoalkanes with react with NaOH or KOH in aqueous conditions in a nucleophilic substitution reaction, whereby the OH^- group replaces the X^- group. A small amount of ethanol is added to help dissolve the halogenoalkane, as they are mostly insoluble in water.

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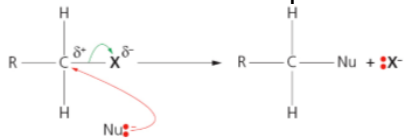
Nucleophilic substitution reactions

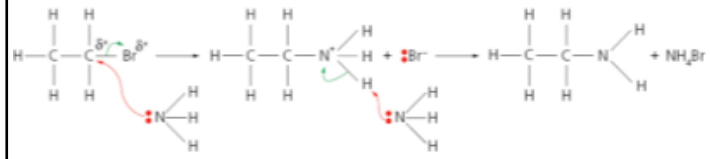
1. Due to the polar nature of the C-X bond, the δ+ carbon is susceptible to nucleophilic attack. Nucleophiles, which are species that can donate a pair of electrons, can be negative ions, such as CN– and OH-, or neutral molecules, such as NH_3 and H_2O. The nucleophile replaces the halogen in a nucleophilic substitution reaction.
2. In general, where Nu is the nucleophile, the nucleophilic substitution mechanism proceeds as shown below:



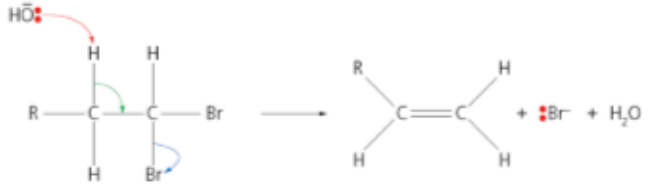
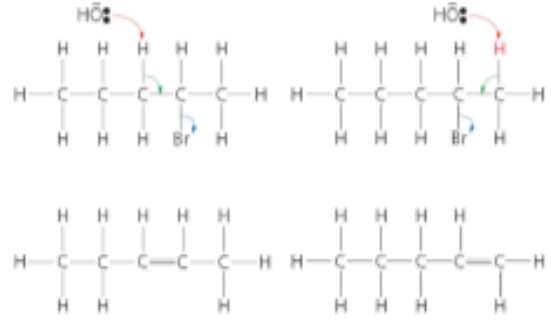
Note that when drawing a mechanism using a negative ion, both the negative charge and the lone pair of electrons must be drawn.

3. The halogen leaves the halogenoalkane in the form of a negative halide ion, and is known as a leaving group.

Reaction with Ammonia

1. Haloalkanes react with concentration ammonia solution according to the following mechanism:
2. 
3. The first ammonia acts as a nucleophile and replaces the Br. The second ammonia acts as a base, and removes an H^+ ion from the N^+. The products are an amine and ammonium bromide.
4. The amine produced when a halogenoalkane reacts with ammonia can react further with another halogenoalkane molecule to form a disubstituted product (and again to form tri– and tetra-substituted products).

Elimination reactions

1. When dissolved in ethanol, the hydroxide ions in NaOH act as a base (not nucleophiles), and remove an H+ from the halogenoalkane in an elimination reaction to form an alkene.
2. 
3. When this reaction is performed on an asymmetric halogenoalkane, two organic products will form, as the hydrogen could be removed from the carbons on either side of the C-X group.
4. 
5. Note that in this example, the isomer on the left would actually give rise to two stereoisomers—the E and Z forms, due to the presence of the carbon-carbon double bond, with each carbon having two different groups attached.

Rates of hydrolysis of the halogenoalkanes with NaOH

1. This table shows that the C-F bond is the strongest of the carbon-halogen bonds. This makes it the most stable bond, and therefore compounds containing this bond are very unreactive compared to those with C-Br or C-I bonds, for example.
This can be tested by reacting three different halogenoalkanes (e.g. CH_3Cl, CH_3Br and CH_3I) with aqueous NaOH in the presence of aqueous $AgNO_3$. When the halide ion is produced, it will form a precipitate of AgX. By timing how long it takes for the precipitate to be produced, the order of the rate of reaction can be found. The order of reactivity (and rate of reaction) is RI > RBr > RCl.

Bond	C–X bond enthalpy/kJ mol^{-1}
C–F	484
C–Cl	338
C–Br	276
C–I	238