HL Answers to Nucleophilic substitution questions

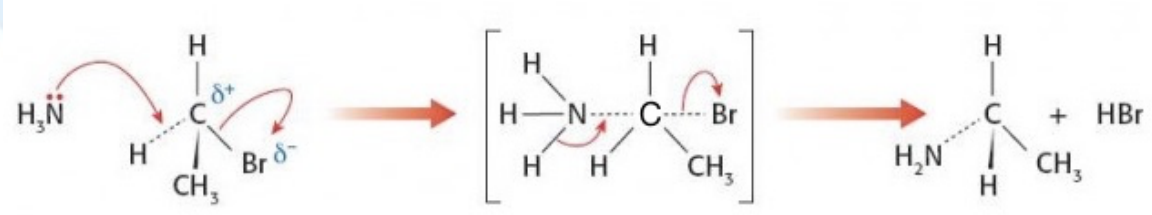
1. i. Both hydroxide ions and water molecules possess non-bonding pairs of electrons but the density of negative charge will be much higher on the ion than on the neutral water molecule. The hydroxide ion will therefore have a greater attraction towards the partially positive carbon atom bonded to the electronegative halogen atom in the halogenoalkanes.

ii. The carbon to iodine bond in iodoethane is much weaker than the carbon to bromine bond in bromoethane so is more easily broken.

iii. 2-bromo-2-methylpropane is a tertiary halogenoalkane. The positive inductive effect of the three methyl groups helps in the formation of an intermediate carbocation so the mechanism is S_N1. The activation energy required to form this carbocation is less than the activation energy required to form the transition state in the S_N2 mechanism for the hydrolysis of the primary halogenoalkane (1-bromobutane).

iv. The carbon to fluorine bond is too strong to be broken.

2.



Note that the reactions of nucleophiles other than the hydroxide ion do not appear to be on the syllabus, so this reaction does not need to be learned. In fact the final product formed will be the substituted ammonia salt, $(C_2H_5)NH_3^+Br^-$ as an acid and a base are present.

3. 1. With primary halogenoalkanes the hydroxide ion is donating a pair of electrons to the carbon atom (which is accepting a pair of electrons) when it forms the transition state.

ii. The second step in the S_N1 mechanism with tertiary halogenoalkanes can also be considered a Lewis acid-base reaction as the intermediate carbocation behaves as a Lewis acid when it accepts a pair of electrons from the hydroxide ion (which is behaving as a Lewis base).

4. React a large excess of bromomethane with ammonia. (Successive nucleophilic substitution reactions will occur and the product will be formed via methylamine, CH_3NH_2, dimethylamine$(CH_3)_2NH$, and trimethylamine, $(CH_3)_3N$.)