FREE RADICAL SUBSTITUTION 2

WHAT HAPPENS	H atoms on alkanes or halogenoalkanes are replaced by halogen atoms (F / Cl / Br / I)

OVERALL EQUATION	For every H atom replaced by F / Cl / Br / I, one molecule of F_2 / Cl_2 / Br_2 / I_2 is used and one molecule of HF / HCl / HBr / HI is released. In order to replace many H atoms with F / Cl / Br / I atoms, an excess of F_2 / Cl_2 / Br_2 / I_2 is used. In order to only replace one H atom, an excess of the alkane / halogenoalkane is used.

e.g. $CH_4 \rightarrow CH_3Cl$ $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

e.g. $CH_4 \rightarrow CF_4$ $CH_4 + 4F_2 \rightarrow CF_4 + 4HF$

e.g. $CH_3\text{-}CBr_3 \rightarrow CBr_3\text{-}CBr_3$ $CH_3\text{-}CBr_3 + 3Br_2 \rightarrow CBr_3\text{-}CBr_3 + 3HBr$

e.g. $CH_2Cl_2 \rightarrow CCl_4$ ……

e.g. $CH_3\text{-}CH_3 \rightarrow CF_3\text{-}CF_3$ ……

e.g. $CHF_2\text{-}CH_3 \rightarrow CBrF_2\text{-}CBr_3$ ……

e.g. $CF_3\text{-}CH_3 \rightarrow CF_3\text{-}CCl_3$ ……

INITIATION	When exposed to ultraviolet light, a molecule of a halogen F_2 / Cl_2 / Br_2 / I_2 breaks apart into two halogen atom free radicals F● / Cl● / Br● / I●. The ultraviolet light provides the energy to break the covalent bond between the two halogen atoms. (Free radicals are species with an odd number of electrons – they are very reactive – the atom with the odd number of electrons is shown with a ●) fluorine: $F_2 \rightarrow 2F\bullet$ bromine: $Br_2 \rightarrow 2Br\bullet$ chlorine: $Cl_2 \rightarrow 2Cl\bullet$ iodine: $I_2 \rightarrow 2I\bullet$

PROPAGATION	(molecule + radical → molecule + radical) For every H that is replaced, there is one pair of propagation reactions. Step 1 the alkane / halogenoalkane reacts with the F● / Cl● / Br● / I● – this removes an H atom from the alkane / halogenoalkane – this produces HF / HCl / HBr / HI and a C based free radical. Step 2 the C based radical from step 1 reacts with F_2 / Cl_2 / Br_2 / I_2 to put an atom of F / Cl / Br / I onto the C based radical – this also produces another halogen free radical (F● / Cl● / Br● / I●) to continue the chain reaction in another step 1.

e.g. $CH_4 \rightarrow CH_3Cl$	(1) $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$ (2) $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
e.g. $CHBr_2\text{-}CH_3 \rightarrow CBr_3\text{-}CH_3$	(1) $CHBr_2\text{-}CH_3 + Br\bullet \rightarrow \bullet CBr_2\text{-}CH_3 + HBr$ (2) $\bullet CBr_2\text{-}CH_3 + Br_2 \rightarrow CBr_3\text{-}CH_3 + Br\bullet$
e.g. $CH_3Cl \rightarrow CH_2Cl_2$	(1) ..... (2) .....
e.g. $CHCl_3 \rightarrow CCl_4$	(1) ..... (2) .....
e.g. $CHF_2\text{-}CH_3 \rightarrow CF_3\text{-}CH_3$	(1) ..... (2) .....
e.g. $CHF_2\text{-}CH_3 \rightarrow CHF_2\text{-}CH_2F$	(1) ..... (2) .....
e.g. $CH_3\text{-}CH_2\text{-}CF_3 \rightarrow CH_3\text{-}CHBr\text{-}CF_3$	(1) ..... (2) .....

TERMINATION	(2 radicals → molecule) If two free radicals collide, they will form a molecule and stop the chain reaction. Any two free radicals involved in the mechanism could collide in this way.

Write an equation to show how each of the molecules shown could be formed by a termination step in the reactions shown.

e.g. $CH_3\text{-}CH_3$ in $CH_4 \rightarrow CH_3Cl$ $\quad 2 \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

e.g. $CCl_3\text{-}CCl_3$ in $CH_4 \rightarrow CCl_4$ $\quad 2 \bullet CCl_3 \rightarrow CCl_3\text{-}CCl_3$

e.g. $CH_2Cl\text{-}CCl_3$ in $CH_4 \rightarrow CCl_4$ $\quad \bullet CH_2Cl + \bullet CCl_3 \rightarrow CH_2Cl\text{-}CCl_3$

e.g. $CF_3\text{-}CH_2F$ in $CH_4 \rightarrow CF_4$ .....

e.g. butane in $CH_3\text{-}CH_3 \rightarrow CH_3\text{-}CH_2F$ .....

e.g. $CBr_3\text{-}CBr_3$ in $CH_4 \rightarrow CBr_4$ .....

e.g. 1,3-dibromobutane in $CH_3\text{-}CH_3 \rightarrow CBr_3\text{-}CBr_3$ .....