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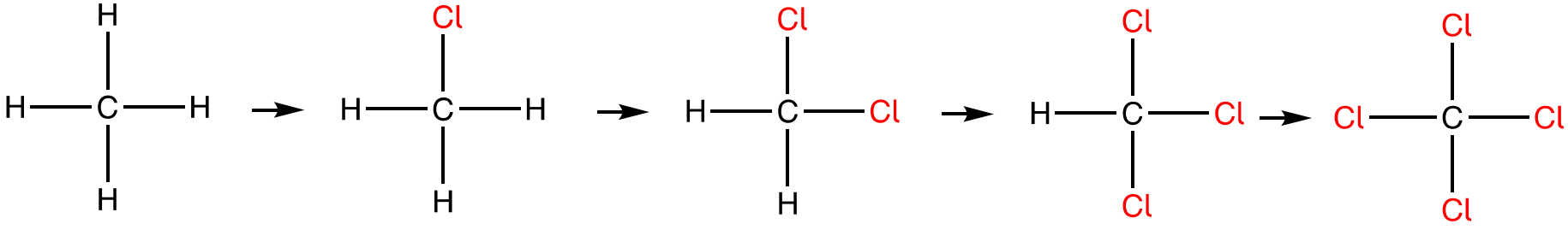
FREE RADICAL SUBSTITUTION

replace H atoms with halogen atoms (F, Cl, Br, I)



by reacting with halogens (F_2, Cl_2, Br_2, I_2) with uv light

- need one molecule of X_2 to replace one H with one X

$CH_4 \rightarrow CH_3Cl$ $\quad$ $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$CH_4 \rightarrow CCl_4$ $\quad$ $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$

$CH_3\text{-}CH_3 \rightarrow CF_3\text{-}CH_3$ $\quad$ $CH_3\text{-}CH_3 + 3F_2 \rightarrow CF_3\text{-}CH_3 + 3HF$

- Use excess alkane to just replace one H atom

$CH_4 \rightarrow CH_3Cl$ Use excess alkane

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

- Use excess X_2 to replace all H atoms

$CH_4 \rightarrow CCl_4$ Use excess Cl_2

$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$

FREE RADICALS

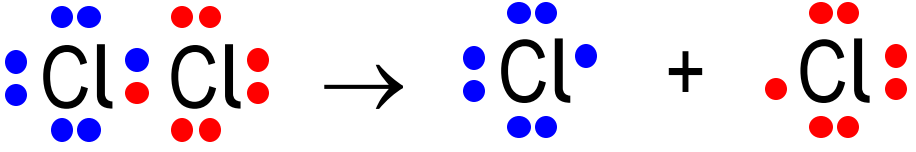
- free radicals have an odd number of electrons
- they are VERY reactive – they react with almost any species they collide with
- we draw free radicals with a • on the atom with the odd number of electrons

e.g. $Cl^{\bullet}$ $^{\bullet}CH_2\text{-}CH_3$ $^{\bullet}OCl$ $CH_3\text{-}\dot{C}H\text{-}CH_3$

INITIATION

- uv light breaks halogen molecules (F_2, Cl_2, Br_2, I_2) into free radicals
- the uv light provides the energy to break the X-X bond

$$Cl_2 \rightarrow 2Cl\bullet$$



INITIATION

$F_2 \rightarrow 2F\bullet$

$Cl_2 \rightarrow 2Cl\bullet$

$Br_2 \rightarrow 2Br\bullet$

$I_2 \rightarrow 2I\bullet$

PROPAGATION

- Halogen radicals react with alkanes in a chain reaction where the halogen radical acts as a catalyst
- For each H replaced, there is a pair of propagation steps

e.g. $CH_4 \rightarrow CH_3Cl$

Step 1 $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$

Step 2 $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

PROPAGATION

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

Step 1 $CH_3\text{-}CH_3 + F\bullet \rightarrow \bullet CH_2\text{-}CH_3 + HF$

Step 2 $\bullet CH_2\text{-}CH_3 + F_2 \rightarrow CH_2F\text{-}CH_3 + F\bullet$

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

Step 1 $CH_2F\text{-}CH_3 + F\bullet \rightarrow CH_2F\text{-}\dot{C}H_2 + HF$

Step 2 $CH_2F\text{-}\dot{C}H_2 + F_2 \rightarrow CH_2F\text{-}CH_2F + F\bullet$

TERMINATION

- When any two free radicals meet they react to form a molecule
- This removes free radicals and stops the chain reaction
- But radical far more likely to meet a molecule than a radical

e.g. $CH_4 \rightarrow CH_3Cl$

free radicals involved $\bullet CH_3$ $Cl\bullet$

$2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

$\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$

NOTE

Initiation molecule → 2 radicals

Propagation molecule + radical → molecule + radical

molecule + radical → molecule + radical

Termination 2 radicals → molecule