



# Organic Chemistry Revision Sheets

## Alkenes | Electrophilic Addition (with Br<sub>2</sub>)

### Reaction

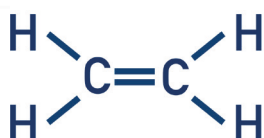
**REACTANTS:** Alkene and Bromine (Br<sub>2</sub>)

**CONDITIONS:** Non-polar organic solvent (or pure liquid bromine)

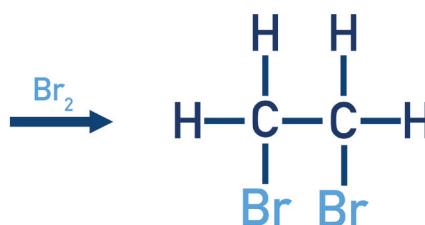
**PRODUCT:** Dibromoalkane

**REACTION TYPE:** Electrophilic Addition

**REACTION:**  
(example of  
ethene)



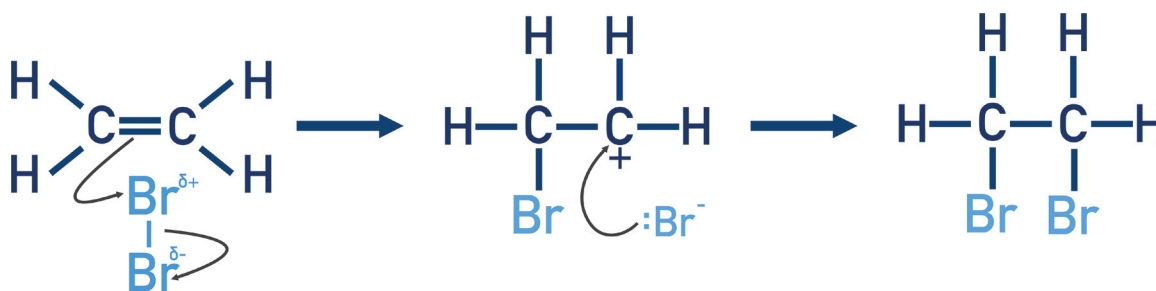
Alkene



Dibromoalkane

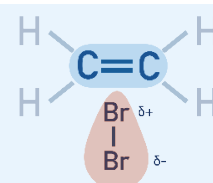
### Mechanism

Br<sub>2</sub> acts as an **electrophile** so the bromine-bromine bond is polarised by the carbon-carbon double bond so the bromine atom with a partial positive charge accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a positively charged carbon (carbocation). The negatively charged bromide ion bonds with the carbocation. Br<sub>2</sub> is 'added' across the double carbon-carbon bond. **Addition reaction.**



### Notes:

- The high electron density in the carbon-carbon double bond (pi-bond) polarises the bromine molecule to create the Br<sup>δ+</sup> electrophile.
- This reaction is often used to identify an alkene as the colour of bromine water changes from orange / brown to colourless when mixed with an alkene (due to the above reaction).





# Organic Chemistry Revision Sheets

## Alkenes | Electrophilic Addition (with HBr)

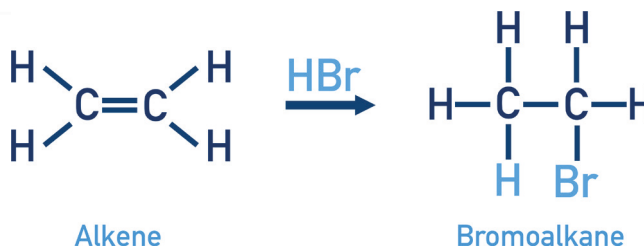
### Reaction

**REACTANTS:** Alkene and HBr (Hydrogen Bromide)

**PRODUCT(S):** Bromoalkane

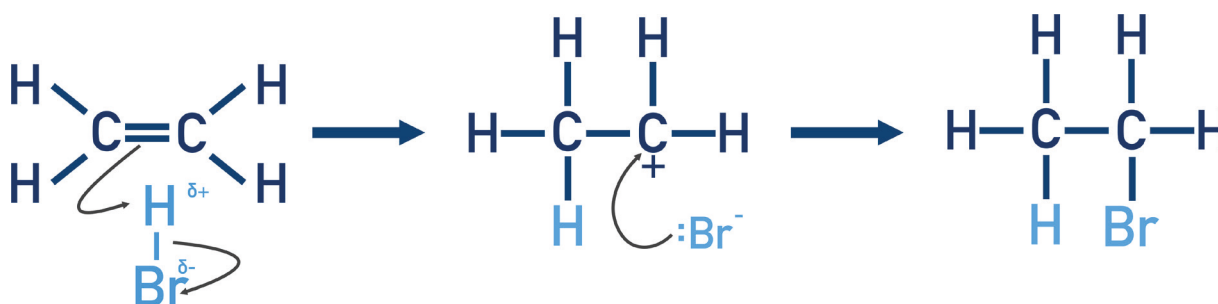
**REACTION TYPE:** Electrophilic Addition

**REACTION:**  
(example of  
ethene)



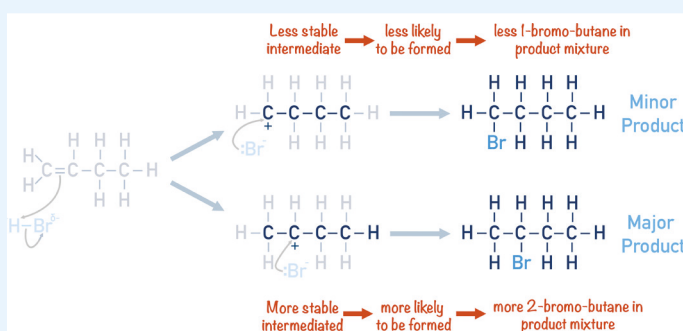
### Mechanism

HBr acts as an **electrophile** because its hydrogen atom (with a partial positive charge) accepts an electron pair from the carbon-carbon double bond. During the reaction the carbon-carbon double bond breaks, forming a positively charged carbon ion (carbocation). The negatively charged bromide ion bonds with the carbocation. HBr is 'added' across the carbon-carbon double bond. **Addition reaction.**



### Notes:

- If a primary or secondary carbocation can be formed during the reaction, **the secondary carbocation will form more readily than the primary carbocation** - creating 'major' and 'minor' products\*.
- The secondary carbocation is more stable due to increased positive inductive effect from neighbouring alkyl chains.
- \*The product mixture will contain more of the major product than the minor product.





# Organic Chemistry Revision Sheets

## Benzene | Electrophilic Substitution, Friedel-Crafts (Acylation)

### Reaction

**REACTANTS:** Benzene and Acyl Chloride

**CONDITIONS:** Warm and  $\text{AlCl}_3$  catalyst

**PRODUCT:** (Aromatic) Ketone

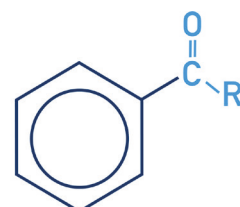
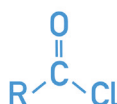
**REACTION TYPE:** Electrophilic Substitution, *Acylation*

**REACTION:**  
(example of  
benzene)



Benzene

+

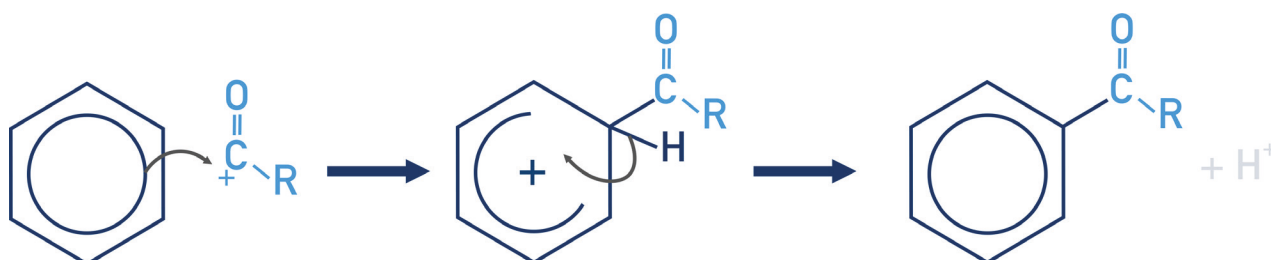


(Aromatic) Ketone

+ HCl

### Mechanism

Acylium ( $\text{RCO}^+$ ) ion **acts as an electrophile due to its carbocation accepting an electron pair** from the delocalised ring of electrons in the benzene ring. A carbon-carbon bond forms. The carbon-hydrogen bond breaks to give the electron pair back to the ring of delocalised electrons.  $\text{RCO}^+$  ion replaces H on benzene ring. **Substitution reaction.**

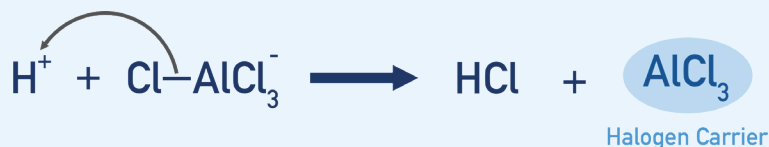


### Notes:

- Acylium ( $\text{RCO}^+$ ) ion is formed by reacting an acyl chloride with a halogen carrier ( $\text{AlCl}_3$ )



- $\text{H}^+$  ion removed from benzene ring combines with  $[\text{AlCl}_4]^-$  to reform  $\text{AlCl}_3$  catalyst and HCl is formed:





# Organic Chemistry Revision Sheets

## Benzene | Electrophilic Substitution, Friedel-Crafts (Alkylation)

### Reaction

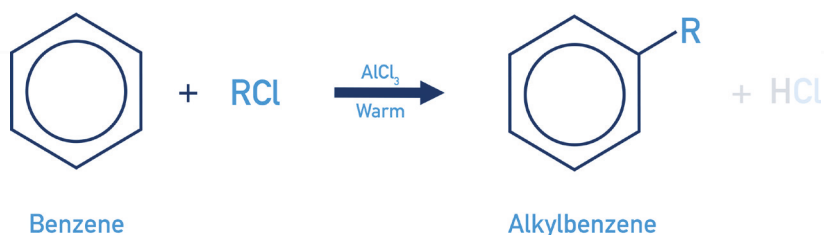
**REACTANTS:** Benzene and Halogenoalkane

**CONDITIONS:** Warm and  $\text{AlCl}_3$  catalyst

**PRODUCT:** Alkylbenzene

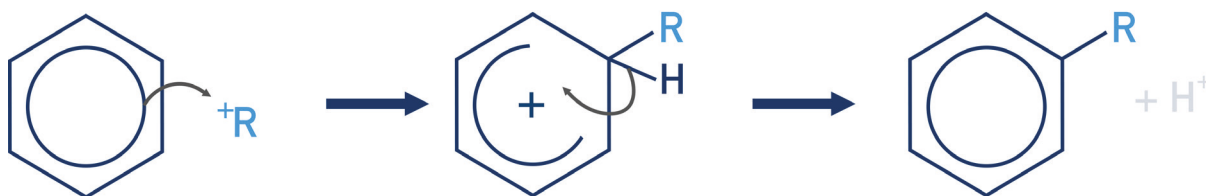
**REACTION TYPE:** Electrophilic Substitution, *Alkylation*

**REACTION:**  
(example of  
benzene)



### Mechanism

Alkyl ( $\text{R}^+$ ) ion **acts as an electrophile due to its carbocation accepting an electron pair** from the delocalised ring of electrons in the benzene ring. Carbon-carbon bond forms. Carbon-hydrogen bond breaks to give electron pair back to delocalised ring of electrons.  $\text{R}^+$  ion replaces H on benzene ring. **Substitution reaction.**



### Notes:

- Alkyl ( $\text{R}^+$ ) ion is formed by reacting a halogenoalkane with a halogen carrier ( $\text{AlCl}_3$ )



- $\text{H}^+$  ion removed from benzene ring combines with  $[\text{AlCl}_4]^-$  to reform  $\text{AlCl}_3$  catalyst and  $\text{HCl}$  is formed







# Organic Chemistry Revision Sheets

## Benzene | Electrophilic Substitution (Halogenation, with Br<sub>2</sub>)

### Reaction

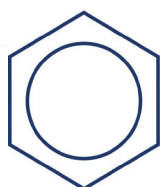
**REACTANTS:** Benzene and Halogen

**CONDITIONS:** Halogen carrier (AlCl<sub>3</sub>, AlBr<sub>3</sub> or Fe)

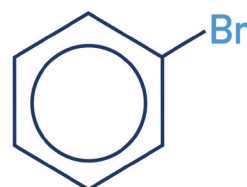
**PRODUCT:** Halogenated Arene (chloro-benzene, bromo-benzene)

**REACTION TYPE:** Electrophilic Substitution, *Halogenation*

**REACTION:**  
(example of  
benzene)



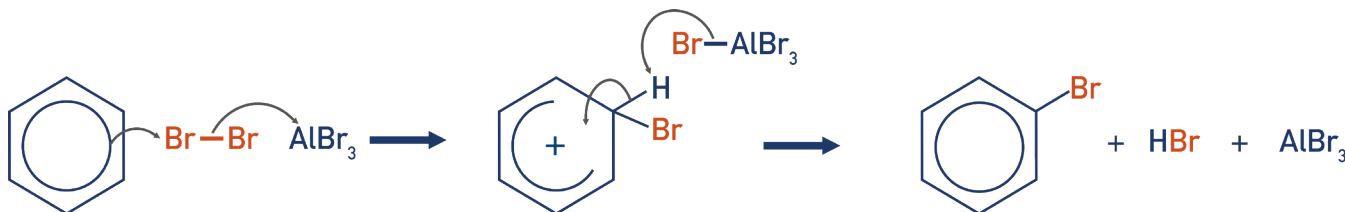
Benzene



Bromobenzene

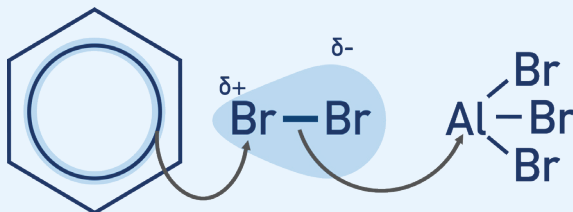
### Mechanism

Bromine molecule **acts as an electrophile** because it is **polarised sufficiently by a halogen carrier (AlBr<sub>3</sub>)** and accepts an electron pair from the delocalised ring of electrons in the benzene ring. A carbon-bromine bond forms. The carbon-hydrogen bond breaks to give the electron pair back to the delocalised ring of electrons. Br replaces H on the benzene ring. **Substitution reaction.**



### Notes:

- Benzene is unable to undergo halogenation without a halogen carrier as the delocalised electron ring is unable to polarise the halogen molecule enough to form an electrophile.
- The halogen carrier polarises the halogen molecule to the point of enabling one of the halogen atoms (now with a partial positive charge) to act as an electrophile and accept a pair of electrons from benzene.





# Organic Chemistry Revision Sheets

## Benzene | Electrophilic Substitution, (Nitration, with $\text{HNO}_3$ )

### Reaction

**REACTANTS:** Benzene and Nitric Acid

**CONDITIONS:**  $55^\circ\text{C}$  and conc. sulfuric acid ( $\text{H}_2\text{SO}_4$ )

**PRODUCT:** Nitrobenzene

**REACTION TYPE:** Electrophilic Substitution, *Nitration*

**REACTION:**  
(example of  
benzene)



Benzene

+

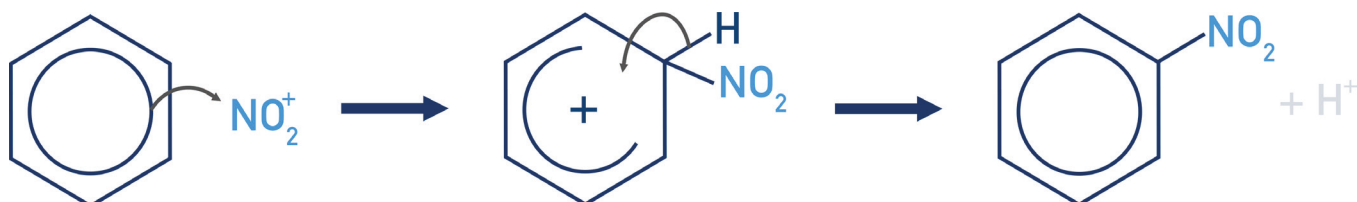
$\text{HNO}_3$



Nitrobenzene

### Mechanism

Nitronium ( $\text{NO}_2^+$ ) ion **acts as an electrophile due to its positively charged nitrogen atom accepting an electron pair** from the delocalised ring of electrons in the benzene ring. A Carbon-nitrogen bond forms. The carbon-hydrogen bond breaks to give electron pair back to delocalised ring of electrons.  $\text{NO}_2^+$  ion replaces H on benzene ring - **substitution reaction**.



### Notes:

- Nitronium ion is formed by the reaction of concentrated nitric acid with concentrated sulfuric acid



Nitronium Ion

- $\text{H}^+$  ion removed from benzene ring combines with hydrogen sulfate ( $\text{HSO}_4^-$ ) ion to reform catalyst  $\text{H}_2\text{SO}_4$ :





# Organic Chemistry Revision Sheets

## Halogenoalkanes | Nucleophilic Substitution (with $\text{NH}_3$ )

### Reaction

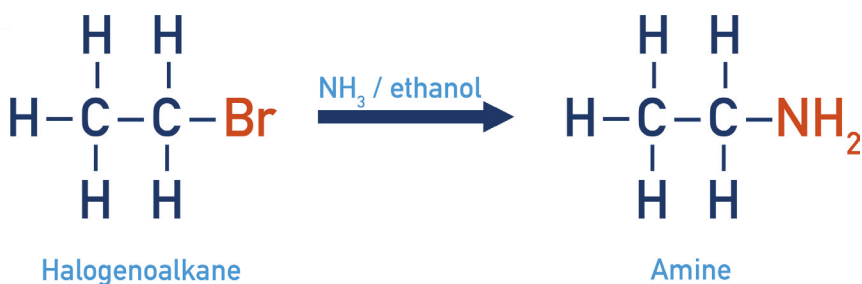
**REACTANTS:** Halogenoalkane and Ammonia ( $\text{NH}_3$ )

**CONDITIONS:** Heat\*, Ethanolic conditions

**PRODUCT(S):** Amine and Ammonium Halide Salt

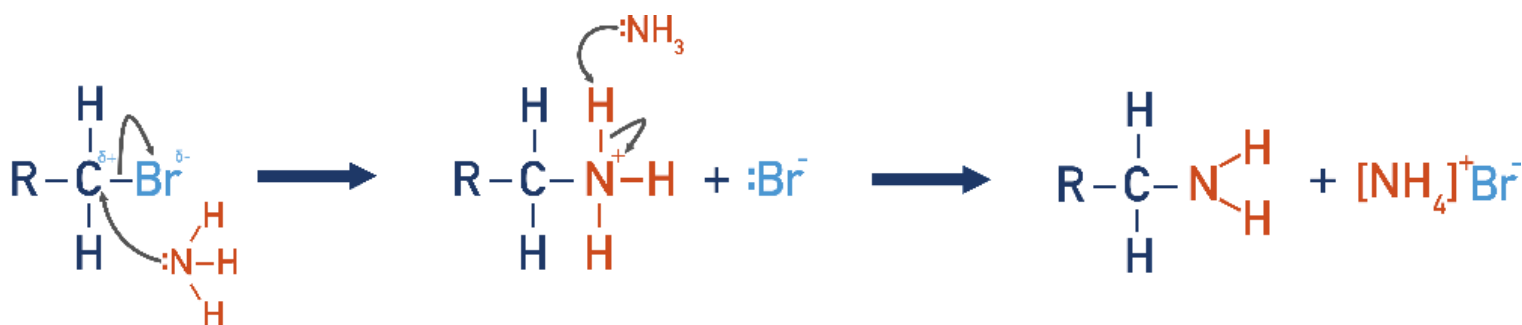
**REACTION TYPE:** Nucleophilic Substitution

**REACTION:**  
(example of  
bromoethane)



### Mechanism

Ammonia ( $\text{NH}_3$ ) acts as a nucleophile, due to its lone pair of electrons on the nitrogen atom and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen bond breaks, forming an (aliphatic) amine and ammonium halide salt.  $\text{NH}_2$  group is **substituted** for the halogen group.



### Notes:

- Reaction must be carried out in **ethanolic conditions (in ethanol, no water present)**, otherwise **an alcohol is likely to form** rather than the nitrile.
- \*A sealed container containing reactants is heated (otherwise ammonia would escape due its high volatility).
- The amine formed in the reaction is actually a stronger base than ammonia, so an ammonium-alkyl salt may be formed. The amine can be obtained by adding sodium hydroxide to the mixture - forcing the amine group to 'release' a  $\text{H}^+$  ion and become a neutral molecule.
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; C-I bond is weakest, giving the fastest reaction.*





# Organic Chemistry Revision Sheets

## Halogenoalkanes | Nucleophilic Substitution (with $\text{OH}^-_{(\text{aq})}$ )

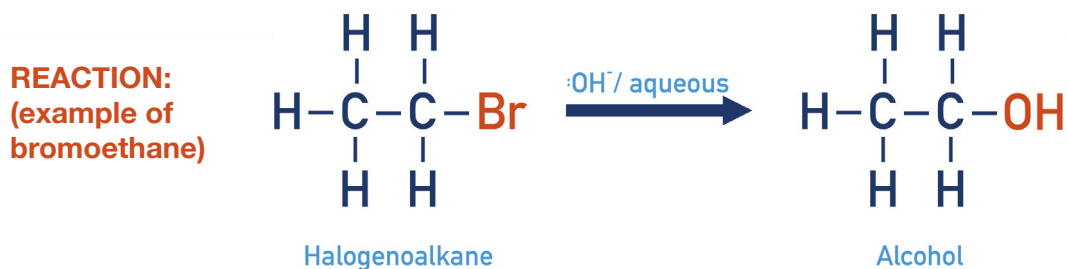
### Reaction

**REACTANTS:** Halogenoalkane and Sodium Hydroxide,  $\text{NaOH}$  (for  $\text{OH}^-$  ions)

**CONDITIONS:** Aqueous ('aq' - water present)

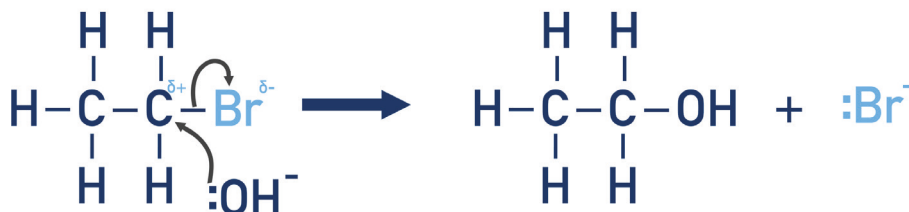
**PRODUCT(S):** Alcohol and Halide Ion (*sodium halide salt if sodium hydroxide used*)

**REACTION TYPE:** Nucleophilic Substitution



### Mechanism

**Hydroxide ion ( $\text{OH}^-$ ) acts as a nucleophile** and attacks the partially positive carbon atom in the carbon-halogen bond. The carbon-halogen breaks, forming alcohol and halide ion.  $\text{OH}$  group is **substituted** for the halogen group.



### Notes:

- Reaction **must be carried out in aqueous conditions (in water), otherwise an elimination reaction will occur and an alkene will be formed.**
- The strength of the carbon-halogen bond (bond enthalpy) determines the speed of the reaction. The stronger the bond, the slower the nucleophilic substitution reaction. *C-F bond is strongest, giving the slowest reaction; C-I bond is weakest, giving the fastest reaction.*



# Organic Chemistry Revision Sheets

## Alkanes | Free Radical Substitution

### Reaction

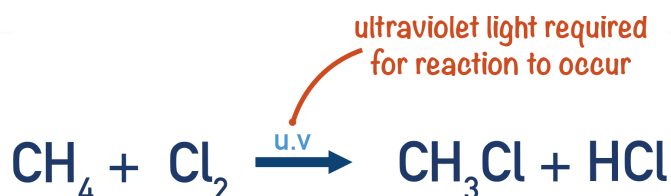
**REACTANTS:** Alkane and Halogen

**CONDITIONS:** U.V (ultraviolet) light

**PRODUCT(S):** Halogenoalkane and Hydrogen Halide

**REACTION TYPE:** Free Radical Substitution

**REACTION:**  
(example of  
methane and  
chlorine)

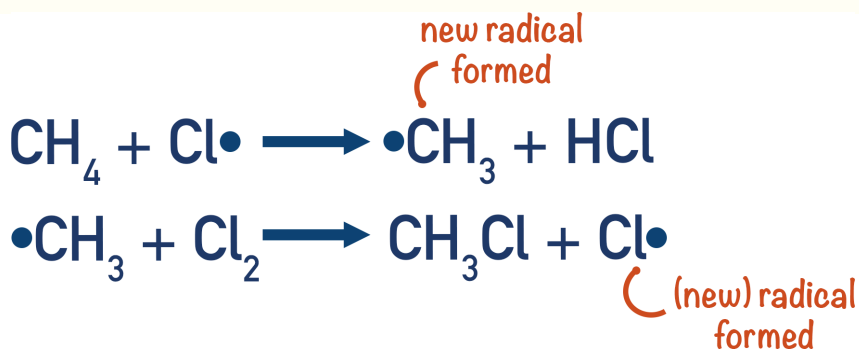


### Mechanism

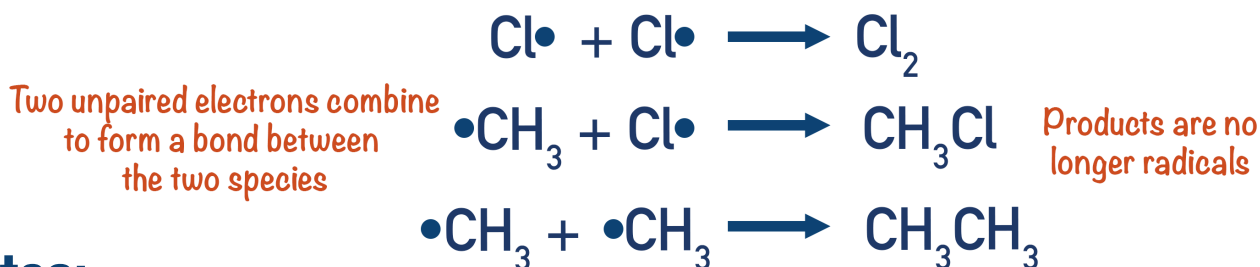
**INITIATION STEP:** Halogen molecule undergoes heterolytic fission to form radical species:



**PROPAGATION STEP:** Radical species reacts with alkane to form alkyl radical and HCl. Alkyl radical then reacts with halogen molecule, reforming another halogen radical, creating a **chain reaction**:



**TERMINATION STEP:** Radical species combine to end chain reaction:



### Notes:

- Heterolytic fission is the even breaking of a covalent bond (each bonded atom gets an electron and becomes a radical species).
- UV light provides the energy required for heterolytic fission.
- Further substitution reactions can occur, eventually forming tetrachloromethane:  
*chloromethane to dichloromethane to trichloromethane to tetrachloromethane*