

Radical and nucleophilic substitution reactions

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Alkanes react with halogens in UV light by free radical substitution, a chain reaction of initiation, propagation and termination. Halogenoalkanes react with nucleophiles in nucleophilic substitution, by SN2 for primary and SN1 for tertiary compounds. Weaker carbon-halogen bonds react faster, so iodoalkanes are the most reactive.

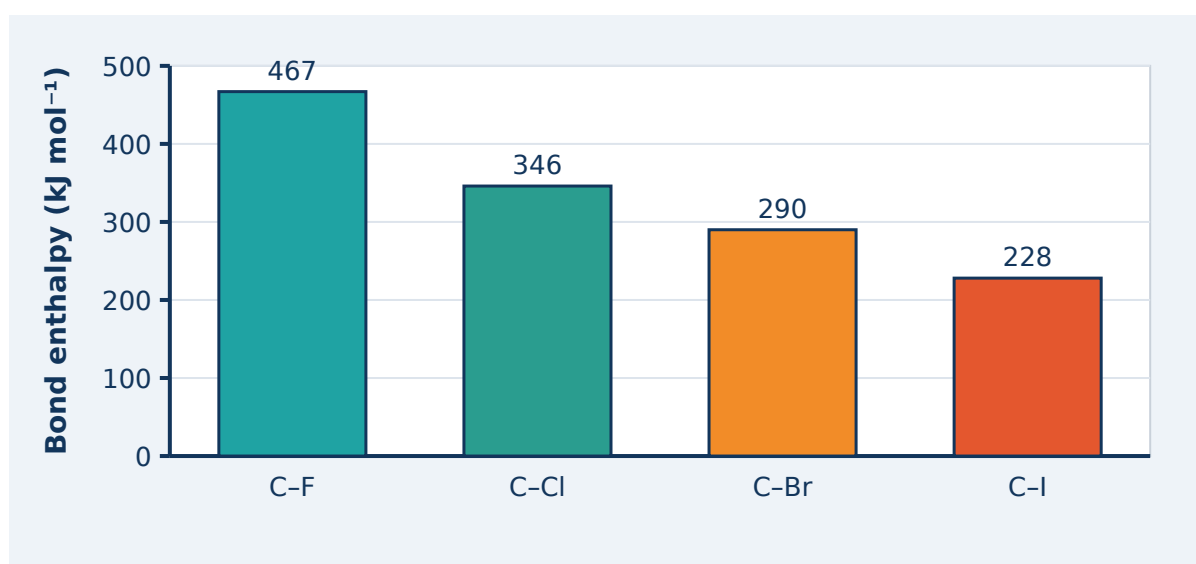
Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R3.4

What are halogenoalkanes and how are they classified?

Halogenoalkanes are alkanes with one or more hydrogen atoms replaced by a halogen. The carbon-halogen bond is polar because the halogen is more electronegative, so the carbon carries a partial positive charge ($\delta+$) that attracts nucleophiles. They are classified by the number of carbon atoms attached to the carbon bearing the halogen: primary (1), secondary (2) and tertiary (3).

Definition

A **nucleophile** is an electron-pair donor. It attacks an electron-deficient ($\delta+$) carbon atom and forms a new covalent bond using its lone pair.

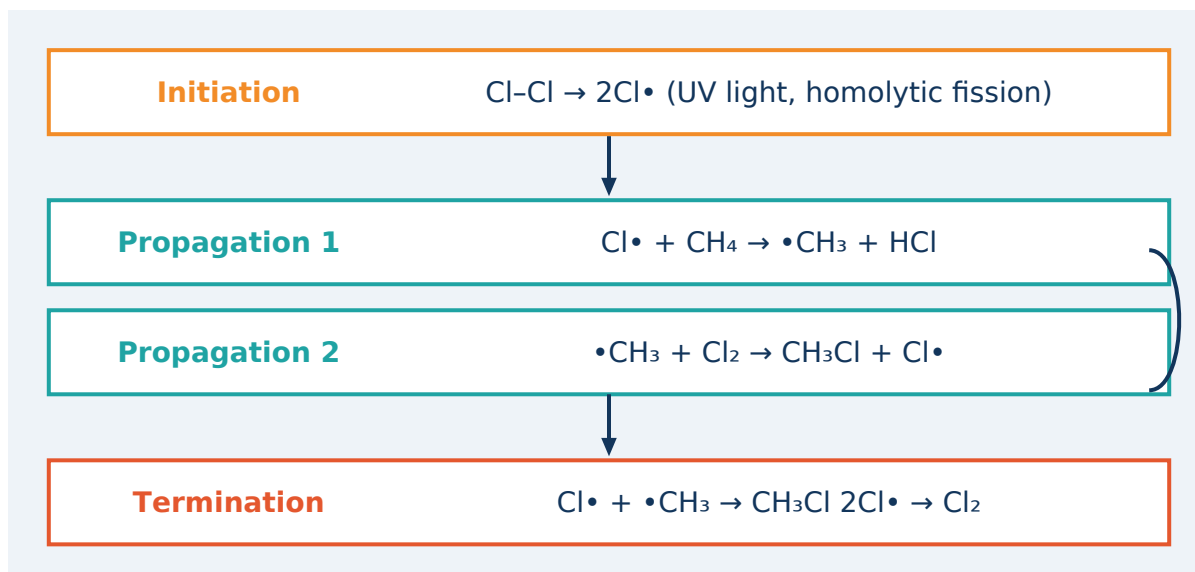


The C-X bond gets weaker down group 7, so iodoalkanes react fastest.

How do alkanes react with halogens?

Alkanes are unreactive, but in UV light they react with chlorine or bromine by free radical substitution. A radical is a species with an unpaired electron, formed by homolytic fission,

where each atom of the broken bond keeps one electron.



The two propagation steps form a chain: each chlorine radical used is made again.

Further substitution gives CH_2Cl_2 , CHCl_3 and CCl_4 , so the product is a mixture. Using excess alkane makes mono-substitution more likely.

Worked example

The Cl-Cl bond enthalpy is 242 kJ mol^{-1} . Calculate the longest wavelength of light that can split one molecule ($h = 6.63 \times 10^{-34} \text{ J s}$, $c = 3.00 \times 10^8 \text{ m s}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$).

Energy per bond = $242\,000 \div 6.02 \times 10^{23} = 4.02 \times 10^{-19} \text{ J}$. $\lambda = hc \div E = (6.63 \times 10^{-34} \times 3.00 \times 10^8) \div 4.02 \times 10^{-19} = 4.95 \times 10^{-7} \text{ m} = \mathbf{495 \text{ nm}}$.

How does nucleophilic substitution work?

In nucleophilic substitution the nucleophile replaces the halogen, which leaves as a halide ion. The conditions decide the product.

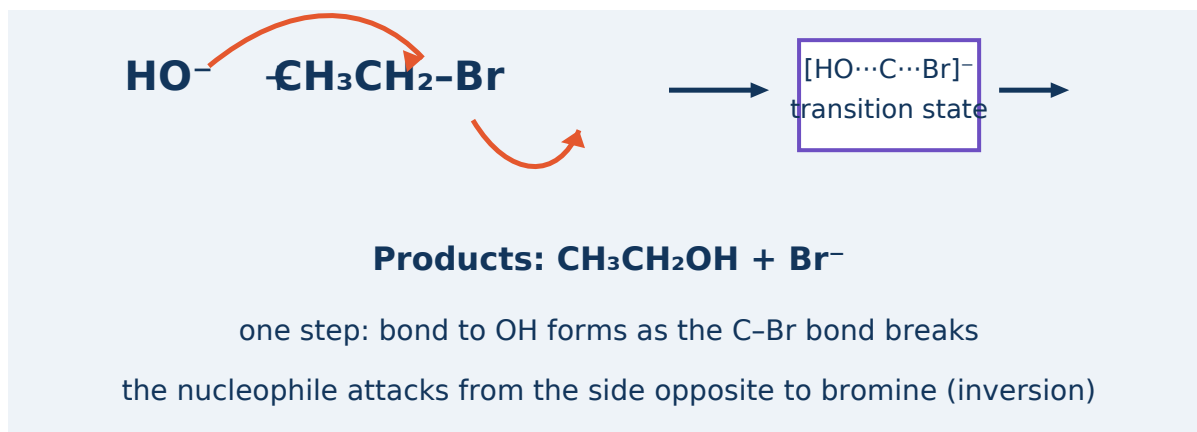
Nucleophile	Conditions	Product (from bromoethane)
OH^-	aqueous NaOH, warm	ethanol, $\text{CH}_3\text{CH}_2\text{OH}$
CN^-	KCN in ethanol, reflux	propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$ (chain longer by one carbon)
NH_3	excess ammonia in ethanol, sealed tube	ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$

With hot ethanolic potassium hydroxide the halogenoalkane loses HBr instead, forming an alkene: this is elimination, and the hydroxide ion acts as a base.

What is the difference between SN1 and SN2?

Primary halogenoalkanes react by SN2: one step, with the nucleophile attacking as the halide leaves. Tertiary halogenoalkanes react by SN1: the halide leaves first to form a planar

carbocation, which is then attacked. Secondary ones can follow either route.



SN2: the first curly arrow shows the lone pair of OH^- attacking carbon, the second shows the C-Br bond breaking to give Br^- .

Feature	SN2	SN1
Steps	one	two (carbocation intermediate)
Rate equation	$\text{rate} = k[\text{RX}][\text{Nu}^-]$	$\text{rate} = k[\text{RX}]$
Typical halogenoalkane	primary	tertiary
Stereochemistry	inversion of configuration	racemic mixture

Key law

The rate of hydrolysis depends on the C-X bond strength: $\text{C-I} > \text{C-Br} > \text{C-Cl}$ in speed, because weaker bonds break more easily. The C-F bond is so strong that fluoroalkanes hardly react.

Worked example

Kofi in Accra warms 5.00 g of 1-bromobutane ($M_r = 136.9$) with aqueous sodium hydroxide and obtains 1.96 g of butan-1-ol ($M_r = 74.0$). Calculate the percentage yield.

$n = 5.00 \div 136.9 = 0.03652 \text{ mol}$; theoretical mass = $0.03652 \times 74.0 = 2.703 \text{ g}$. Yield = $1.96 \div 2.703 \times 100 = \mathbf{72.5\%}$.

How can you compare the rates of hydrolysis?

Warm the halogenoalkane with ethanolic silver nitrate. Water slowly hydrolyses it, releasing halide ions that precipitate at once as AgCl (white), AgBr (cream) or AgI (yellow). The shorter the time to a precipitate, the faster the hydrolysis. Iodoalkanes give a precipitate first, then bromo, then chloro.

Why do CFCs damage the ozone layer?

In the stratosphere UV breaks the C-Cl bond in CFCs to give $\text{Cl}\cdot$ radicals, which catalyse ozone destruction: $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$ and $\text{ClO}\cdot + \text{O} \rightarrow \text{Cl}\cdot + \text{O}_2$. The chlorine radical is

regenerated, so one radical can destroy thousands of ozone molecules.

Common mistake

Do not confuse the roles of hydroxide. With aqueous NaOH it is a nucleophile and gives an alcohol; with ethanolic KOH and heat it is a base and gives an alkene. The solvent changes the product.

Lina's tip

Draw curly arrows from a lone pair or bond to where electrons end up. The nucleophile arrow starts at the lone pair and points to the δ^+ carbon; the second arrow starts at the C-X bond and points to the halogen.

Key points to remember

- Free radical substitution: initiation, propagation, termination; needs UV light
- Nucleophile = electron-pair donor: OH^- gives alcohols, CN^- nitriles, NH_3 amines
- $\text{S}_\text{N}2$: one step, rate = $k[\text{RX}][\text{Nu}]$, inversion; $\text{S}_\text{N}1$: carbocation, rate = $k[\text{RX}]$, racemic
- C-X bond enthalpy: C-F 467, C-Cl 346, C-Br 290, C-I 228 kJ mol^{-1}
- Ethanolic KOH and heat causes elimination to an alkene

Radical and nucleophilic substitution reactions: frequently asked questions

Why do iodoalkanes react faster than chloroalkanes?

The C-I bond is longer and weaker (228 kJ mol^{-1}) than the C-Cl bond (346 kJ mol^{-1}). Less energy is needed to break it, so substitution is faster.

What is a free radical?

It is a species with an unpaired electron, such as $\text{Cl}\cdot$. It forms when a covalent bond splits evenly in homolytic fission, usually in UV light.

How do $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanisms differ?

$\text{S}_\text{N}2$ happens in one step and its rate depends on both reactants, while $\text{S}_\text{N}1$ has a carbocation intermediate and its rate depends only on the halogenoalkane. $\text{S}_\text{N}2$ inverts the configuration and $\text{S}_\text{N}1$ gives a racemic mixture.

Why is ethanol used as the solvent for the cyanide reaction?

Water would also act as a nucleophile and form an alcohol as a by-product. Ethanol keeps the nucleophile as the cyanide ion only.

Why is excess ammonia used to make amines?

The amine product is also a nucleophile and could react further with the halogenoalkane. A large excess of ammonia makes the primary amine the main product.