

# Reactivity 3.3 · Electron sharing reactions

## · supported focus

International Baccalaureate · IB Diploma · Chemistry · SL

### Scope and prerequisites

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Supported SL core focus. First assessment 2025; current brief acquired; full Chemistry guide not acquired. Remaining guide, assessment and practical requirements retain their recorded holds.

Prerequisites: covalent bonding from Structure 2.2 and alkane structure from Structure 3.2. Each lesson develops its own method before independent transfer.

These are original or explicitly fictional teaching examples, not actual measurements or completed assessed learner investigations.

### Electron sharing reactions

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#### ■ What would explain this observation?

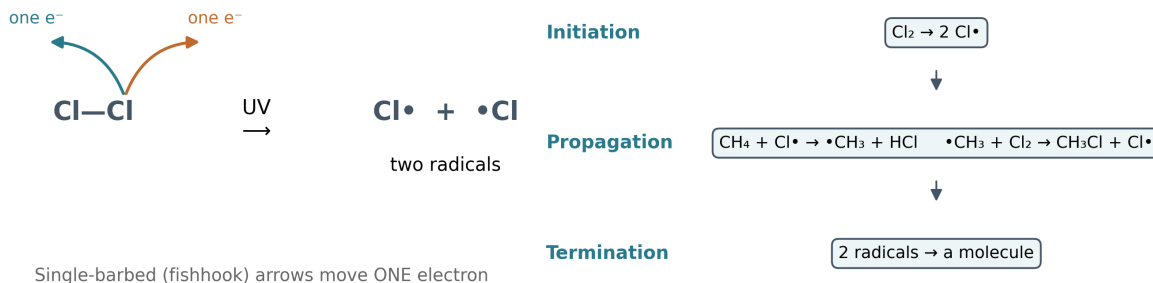
- Methane and chlorine are mixed in the dark and nothing happens; the same mixture in sunlight reacts at once, and the product is never pure chloromethane – it always carries further-substituted molecules. Why?
  - Start with a prediction. State the quantities or features you would compare, then decide what evidence could distinguish two explanations.
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#### ■ Build the model

- A covalent bond can break by **homolytic fission** : the shared pair splits so each atom keeps one electron, forming two **free radicals** – atoms or groups with an unpaired electron, written with a dot, such as  $\text{Cl}\cdot$ . A single-barbed (fishhook) arrow shows ONE electron moving.
- Radical substitution runs as a chain: **initiation** (UV light splits  $\text{Cl}_2$  into two  $\text{Cl}\cdot$ ), **propagation** (a radical makes a product and another radical:  $\text{CH}_4 + \text{Cl}\cdot \rightarrow \cdot\text{CH}_3 + \text{HCl}$ , then  $\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$ ), and **termination** (two radicals join, ending the chain).
- homolytic fission: Bond breaking that gives each atom one electron of the shared pair; free radical: A species with an unpaired electron, highly reactive; initiation: The step that first produces radicals; propagation: A chain step consuming one radical and producing another; termination: A step removing radicals by joining two of them.

Homolytic fission: one electron to each atom

Radical chain substitution



## ■ Choose evidence that can test it

- The reaction needs UV light or heat to start but then continues on its own – evidence for a chain in which each step regenerates a radical. Trace amounts of ethane among the products show that two  $\cdot\text{CH}_3$  radicals joined in a termination step.
- A mixture of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  forms because the product still has C–H bonds open to further propagation; single-substitution purity is evidence against a controlled, non-chain route.

## ■ Work from known quantities

- State the known values and their units. Choose the relation because its assumptions fit this case, then rearrange before substitution.
- Known: the bond enthalpies are  $\text{Cl}-\text{Cl}$  242 kJ/mol and  $\text{C}-\text{H}$  413 kJ/mol. Bond breaking is endothermic, so the weaker bond breaks first. Comparing the two:  $413 - 242 = 171$  kJ/mol less energy breaks  $\text{Cl}-\text{Cl}$ , which is why UV initiates the chain by splitting chlorine rather than methane.

### Example:

The  $\text{H}-\text{Cl}$  bond enthalpy is 431 kJ/mol and the  $\text{C}-\text{Cl}$  bond in  $\text{CH}_3\text{Cl}$  is 339 kJ/mol. For the propagation step  $\text{CH}_4 + \text{Cl}\cdot \rightarrow \cdot\text{CH}_3 + \text{HCl}$ , estimate the energy change using the same sequence: known quantities  $\rightarrow$  model  $\rightarrow$  relation  $\rightarrow$  substitution  $\rightarrow$  unit and interpretation. (Answer: break  $\text{C}-\text{H}$  (+413), form  $\text{H}-\text{Cl}$  (–431):  $\Delta H \approx 413 - 431 = -18$  kJ/mol – slightly exothermic, so the step proceeds readily once radicals exist.)

## ■ Check the conclusion and its limits

- Bond enthalpies are averages measured over many compounds, so an estimate from them is approximate, not exact. The chain model for this reaction explains the UV start and the product mixture; it does not describe polar reagents, where heterolytic (electron-PAIR) mechanisms apply instead – the next lesson’s model.
- Return to the original observation. Explain what the result supports, which conditions it assumes, and one way to test a competing explanation.

### Warn:

In a radical substitution, every chlorine atom ends up substituted onto a methane molecule. This claim is false: termination joins radicals with each other ( $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$ , or two  $\cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ), and propagation continues substituting the products, so the outcome is always a mixture.

### Key:

Electron sharing reactions: homolytic fission splits a shared pair one electron each way, giving radicals; fishhook arrows track single electrons. Radical substitution chains through initiation, propagation and termination, which explains the UV trigger and the mixture of products.