

Electron sharing reactions

Reactivity 3.3 · SL

Why does sunlight matter?

Light makes radicals, and radicals start a chain.

- Methane and chlorine in the dark do nothing.
- In sunlight they react at once, giving several products.
- This unit: radicals → **homolytic fission** → chain reactions → **ozone**.

What a radical is

- A dot marks the **unpaired electron**.
- Radicals are very reactive.

Radical a particle with an unpaired electron, such as $\text{Cl}\bullet$, $\bullet\text{CH}_3$ or $\bullet\text{OH}$

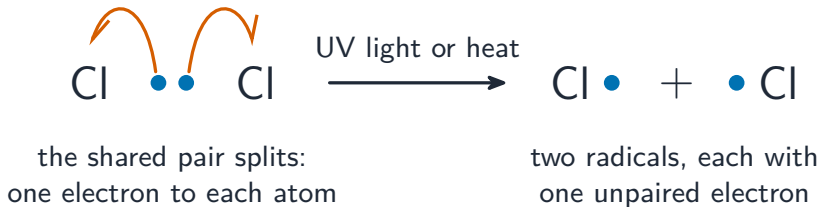
Check: radical or ion?

Your turn

Which particle is a radical?

- A. Cl^-
- B. CH_4
- C. $\bullet\text{CH}_3$
- D. OH^-

Homolytic fission



Homolytic fission always makes two radicals.

Which bond breaks?

Bond	Bond enthalpy / kJ mol^{-1}
Br-Br	193
Cl-Cl	242
C-C	346
C-H	414

Use the evidence

In $\text{CH}_4 + \text{Cl}_2$, UV splits Cl-Cl.

Why alkanes are unreactive

Strong bonds

C–C 346 and C–H 414 kJ mol⁻¹.

Breaking them needs a lot of energy.

Almost non-polar

C 2.6 and H 2.2 electronegativity.

Nothing attracts a charged reagent.

The chain reaction

1. initiation



UV light splits the weakest bond, Cl–Cl, into two radicals

2. propagation

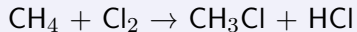


each step uses a radical and makes a new one, so the chain continues

3. termination



two radicals join, so the chain ends



Naming the stage

Radicals left	Radicals right	Stage
0	2	initiation
1	1	propagation
2	0	termination

Why a mixture forms

More CH_3Cl

Large excess of methane.

$\text{Cl}\bullet$ usually meets CH_4 .

More CCl_4

Large excess of chlorine.

Substitution keeps going.

Evidence for a chain

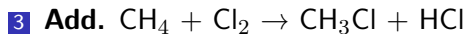
Each radical is passed on many times before **termination**.

- Nothing happens in the dark.
- A short flash of light causes a lot of reaction.
- Traces of ethane appear, from two $\bullet\text{CH}_3$ joining.

Energy of the propagation steps

1 Step 1. $414 - 431 = -17 \text{ kJ mol}^{-1}$

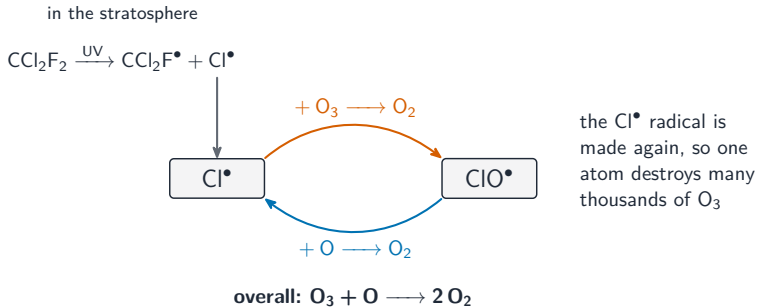
2 Step 2. $242 - 324 = -82 \text{ kJ mol}^{-1}$



Decision

$\Delta H = -99 \text{ kJ mol}^{-1}$; both steps exothermic

How CFCs destroy ozone



One Cl atom can destroy many thousands of O_3 molecules.

Exam tips

A mixture forms because the product still has C–H bonds.

- Always draw the dot, on the atom with the **unpaired electron**.
- First propagation step gives $\bullet\text{CH}_3 + \text{HCl}$.
- Single barb, one electron; double barb, a pair.
- **Termination** has two radicals on the left, none on the right.

Check yourself

Try these

Write the homolytic fission of bromine and state the condition.

Write the mechanism for ethane + chlorine, with a termination step that forms butane.

Find ΔH for each propagation step in the bromination of methane.

Explain with equations how one Cl atom destroys many O_3 molecules.