

Radical and nucleophilic substitution reactions

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

Each answer shows the equation or method and the result in bold. In mechanisms, check where the curly arrows start and finish, and in calculations check the mole ratios and the units.

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

Problem 1 Nucleophiles

1. A species that **donates a lone pair** of electrons to form a covalent bond.
2. **H₂O**, **OH⁻** and **NH₃** (BF₃ and H⁺ accept electrons; Cl• is a radical).

Problem 2 Primary, secondary or tertiary

Primary; secondary; tertiary; primary (count the carbons attached to the carbon bearing the halogen).

Problem 3 Products of bromoethane

1. **ethanol**, nucleophilic substitution.
2. **propanenitrile**, nucleophilic substitution.
3. **ethylamine**, nucleophilic substitution.
4. **ethene**, elimination.

Problem 4 Radicals

1. Breaking of a covalent bond so that each atom takes **one of the bonding electrons**.
2. **Br₂ → 2Br•**.
3. A species with an **unpaired electron**.

Problem 5 Chlorinating methane

1. **CH₄ + Cl₂ → CH₃Cl + HCl**.
2. Dichloromethane, trichloromethane and tetrachloromethane, because chlorine keeps replacing hydrogen.
3. **CH₄ + 4Cl₂ → CCl₄ + 4HCl**.

Problem 6 Bond enthalpies and rate

1. **iodo > bromo > chloro > fluoro**.

2. AgI yellow, AgBr cream, AgCl white; fluoro gives none (AgF is soluble).
3. Bond strength, not polarity, controls the rate: the C-F bond is so strong that breaking it is the slow step.

Problem 7 Ethane and bromine

1. $\text{CH}_3\text{CH}_3 + \text{Br}\cdot \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{HBr}$; $\text{CH}_3\text{CH}_2\cdot + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{Br}\cdot$.
2. $\text{Br}\cdot + \text{Br}\cdot \rightarrow \text{Br}_2$; $\text{CH}_3\text{CH}_2\cdot + \text{Br}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Br}$; $2\text{CH}_3\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.
3. Two ethyl radicals sometimes meet and combine, forming **butane** by termination.

Problem 8 Percentage yield

1. $\text{CH}_3\text{CHBrCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{NaBr}$.
2. $n = 8.00 \div 122.9 = 0.06509 \text{ mol}$; $\text{mass} = 0.06509 \times 60.0 = \mathbf{3.906 \text{ g}}$.
3. $\text{Yield} = 2.81 \div 3.906 \times 100 = \mathbf{71.9 \%}$.

Problem 9 Rate data for 1-bromopropane

1. Doubling [RBr] doubles the rate: first order. Tripling $[\text{OH}^-]$ triples the rate: first order.
2. $\text{rate} = k[\text{RBr}][\text{OH}^-]$; $k = 2.0 \times 10^{-4} \div (0.10 \times 0.10) = \mathbf{2.0 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$.
3. Both reactants are in the rate equation, so it is **SN2**.

Problem 10 Ozone destruction

1. $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$ and $\text{ClO}\cdot + \text{O} \rightarrow \text{Cl}\cdot + \text{O}_2$.
2. $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$; $\text{Cl}\cdot$ is a catalyst.
3. $E = 346\,000 \div 6.02 \times 10^{23} = 5.75 \times 10^{-19} \text{ J}$; $\lambda = (6.63 \times 10^{-34} \times 3.00 \times 10^8) \div 5.75 \times 10^{-19} = \mathbf{346 \text{ nm}}$, in the ultraviolet region.

Problem 11 Making an amine

1. $10.89 \div 108.9 = \mathbf{0.1000 \text{ mol}}$.
2. $n(\text{NH}_3) = 0.200 \text{ mol}$; $\text{mass} = 0.200 \times 17.0 = \mathbf{3.40 \text{ g}}$.
3. The product amine is also a nucleophile and could react further to give $(\text{CH}_3\text{CH}_2)_2\text{NH}$; excess NH_3 makes this unlikely.

Problem 12 Elimination

1. $\text{CH}_3\text{CHBrCH}_2\text{CH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{KBr} + \text{H}_2\text{O}$.
2. **but-1-ene, Z-but-2-ene and E-but-2-ene**.
3. Elimination uses ethanolic KOH and heat; substitution uses aqueous NaOH, warm.

Problem 13 Silver nitrate test times

1. $40 \div 8 = \mathbf{5.0 \text{ times faster}}$.

2. The C-I bond is weaker than C-Br and C-Cl, so it breaks most easily and gives halide ions first.

Problem 14 Spot the errors

1. Substitution is **stepwise**: CH_3Cl , CH_2Cl_2 and CHCl_3 form first.
2. OH^- is a **nucleophile** (a lone pair donor).
3. $\text{S}_\text{N}2$ causes **inversion** of configuration; $\text{S}_\text{N}1$ gives the racemic mixture.

Problem 15 Atom economy and mass

1. $M_r \text{CH}_3\text{Cl} = 50.5$; reactants = $16.0 + 71.0 = 87.0$; atom economy = $50.5 \div 87.0 \times 100 = \mathbf{58.0\%}$.
2. $n(\text{CCl}_4) = 100 \div 154.0 = 0.6494 \text{ mol}$; $n(\text{Cl}_2) = 2.597 \text{ mol}$; mass = $2.597 \times 71.0 = \mathbf{184 \text{ g}}$.

Problem 16 Tertiary halogenoalkane

1. Rate is first order in RBr and zero order in OH^- : rate = $k[\text{RBr}]$; $k = 3.0 \times 10^{-5} \div 0.10 = \mathbf{3.0 \times 10^{-4} \text{ s}^{-1}}$.
2. $t_{1/2} = \ln 2 \div k = 0.693 \div 3.0 \times 10^{-4} = \mathbf{2.31 \times 10^3 \text{ s}}$ (38.5 min).
3. Three alkyl groups push electrons toward the positive carbon (inductive effect), stabilising the tertiary carbocation.

Problem 17 Stereochemistry and profiles

1. **B is $\text{S}_\text{N}1$** : two peaks with a valley, the carbocation intermediate; A has a single peak (one step, $\text{S}_\text{N}2$).
2. $\text{S}_\text{N}2$ inverts the configuration, giving a **single enantiomer**, so the product is still optically active.
3. The carbocation is planar, so water attacks equally from both faces, forming a **racemic mixture** with no net rotation.

Problem 18 Enthalpy of chlorination

1. Broken $413 + 242 = 655$; made $346 + 432 = 778$; $\Delta H = 655 - 778 = \mathbf{-123 \text{ kJ mol}^{-1}}$.
2. $\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot\text{CH}_3$: $413 - 432 = \mathbf{-19}$; $\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$: $242 - 346 = \mathbf{-104}$; sum -123 .
3. A chlorine radical is regenerated at every cycle, so the chain repeats until radicals terminate.

Problem 19 Two-step synthesis

1. Step 1: **KCN in ethanol, reflux**; step 2: **dilute HCl, reflux**.
2. With water present OH^- could compete and form ethanol; ethanol avoids this.
3. $\mathbf{\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}}$.

Problem 20 CFCs and HFCs

1. $M_r = 12.0 + 19.0 + 106.5 = 137.5$; $Cl = 106.5 \div 137.5 \times 100 = \mathbf{77.5\%}$.
2. $E = 467\,000 \div 6.02 \times 10^{23} = 7.76 \times 10^{-19} \text{ J}$; $\lambda = 1.989 \times 10^{-25} \div 7.76 \times 10^{-19} = \mathbf{256 \text{ nm}}$, shorter than for C-Cl.
3. The C-F bond is stronger, and HFCs contain no chlorine to give $\text{Cl}\cdot$ radicals that catalyse ozone destruction.