

Radical and nucleophilic substitution reactions

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

Name: _____ Date: _____ Class: _____

These 20 problems cover free radical substitution, nucleophilic substitution and elimination, SN1 and SN2 mechanisms, and the effect of bond enthalpy on rate. You will balance equations, interpret rate data and calculate yields.

They suit A Level, IB Chemistry, CBSE Class 11-12 and WAEC or NECO senior students. Show your steps and give units.

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

Problem 1 Nucleophiles (easy)

1. State what is meant by a nucleophile.
2. Identify the nucleophiles from: H_2O , BF_3 , OH^- , H^+ , NH_3 , $\text{Cl}^\bullet$.

Problem 2 Primary, secondary or tertiary (easy)

Classify each as primary, secondary or tertiary: 1-chloropropane, 2-bromopropane, 2-bromo-2-methylpropane, 1-iodo-2-methylpropane.

Problem 3 Products of bromoethane (easy)

Name the organic product and the type of reaction when bromoethane reacts with:

1. warm aqueous NaOH
2. KCN in ethanol, reflux
3. excess ammonia in ethanol, sealed tube
4. hot ethanolic KOH

Problem 4 Radicals (easy)

1. Define homolytic fission.
2. Write the equation for the initiation step of bromine in UV light.
3. State what is meant by a radical.

Problem 5 Chlorinating methane (easy)

1. Write the equation for methane and chlorine forming chloromethane.
2. Name the other products that can form.

3. Write the equation for forming tetrachloromethane.

Problem 6 Bond enthalpies and rate (medium)

Bond enthalpies: C-F 467, C-Cl 346, C-Br 290, C-I 228 kJ mol⁻¹.

1. Rank the four 1-halobutanes by rate of hydrolysis, fastest first.
2. Give the colour of the silver halide precipitate for each that gives one.
3. Explain why C-F is the slowest although it is the most polar bond.

Problem 7 Ethane and bromine (medium)

Ethane reacts with bromine in UV light.

1. Write the two propagation steps.
2. Write three termination steps.
3. Explain why a small amount of butane is also found.

Problem 8 Percentage yield (medium)

Wanjiru warms 8.00 g of 2-bromopropane ($M_r = 122.9$) with aqueous NaOH and collects 2.81 g of propan-2-ol ($M_r = 60.0$).

1. Write the equation.
2. Calculate the theoretical mass.
3. Calculate the percentage yield.

Problem 9 Rate data for 1-bromopropane (medium)

Rates for 1-bromopropane with OH⁻ at constant temperature: [RBr] 0.10, [OH⁻] 0.10, rate 2.0×10^{-4} ; [RBr] 0.20, [OH⁻] 0.10, rate 4.0×10^{-4} ; [RBr] 0.10, [OH⁻] 0.30, rate 6.0×10^{-4} (concentrations in mol dm⁻³, rate in mol dm⁻³ s⁻¹).

1. Deduce the order for each reactant.
2. Write the rate equation and calculate k with units.
3. State the mechanism.

Problem 10 Ozone destruction (medium)

A CFC releases Cl• in the stratosphere.

1. Write the two propagation steps that destroy ozone, O₃, with oxygen atoms O.
2. Write the overall equation.
3. Calculate the longest wavelength that can break a C-Cl bond (346 kJ mol⁻¹; $h = 6.63 \times 10^{-34}$ J s, $c = 3.00 \times 10^8$ m s⁻¹, $N_A = 6.02 \times 10^{23}$ mol⁻¹).

Problem 11 Making an amine (medium)

Bilal reacts 10.89 g of bromoethane ($M_r = 108.9$) with ammonia: $\text{CH}_3\text{CH}_2\text{Br} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$.

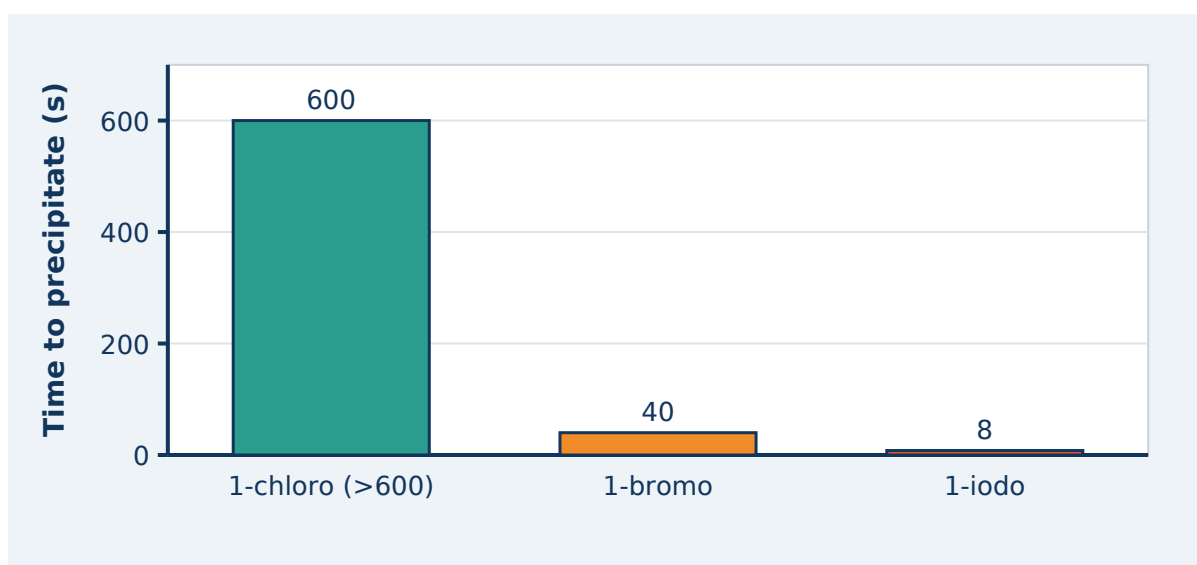
1. Calculate $n(\text{bromoethane})$.
2. Calculate the minimum mass of NH_3 ($M_r = 17.0$).
3. Explain why a large excess of ammonia is used.

Problem 12 Elimination (medium)

2-bromobutane is heated with ethanolic potassium hydroxide.

1. Write the equation for forming but-2-ene.
2. Name all possible alkene products.
3. State how the conditions differ from those for substitution.

Problem 13 Silver nitrate test times (medium)



Time for a precipitate with warm ethanolic silver nitrate.

The figure shows the times for 1-halobutanes to give a precipitate with warm ethanolic silver nitrate.

1. Calculate how many times faster 1-iodobutane reacts than 1-bromobutane ($\text{rate} \propto 1 \div \text{time}$).
2. Explain the order of rates.

Problem 14 Spot the errors (medium)

Chiamaka in Lagos wrote three statements. Identify and correct each error.

1. CCl_4 is made in one step from methane and chlorine.
2. Hydroxide is an electrophile in hydrolysis.
3. $\text{S}_\text{N}2$ gives a racemic mixture.

Problem 15 Atom economy and mass (medium)

Chloromethane is made by $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$.

1. Calculate the atom economy for CH_3Cl (A_r : C 12.0, H 1.0, Cl 35.5).

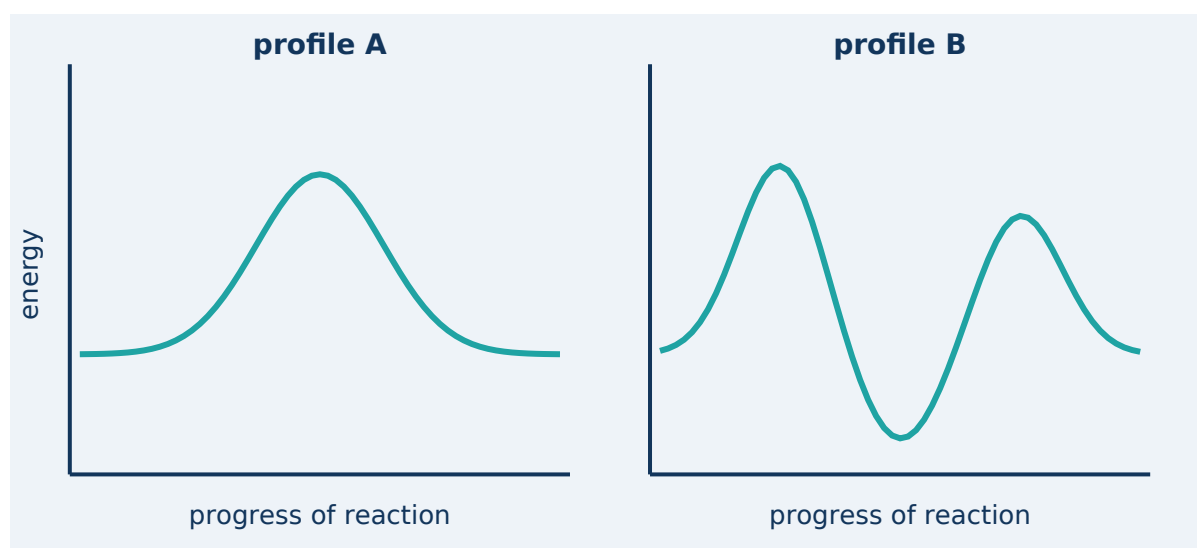
2. Calculate the mass of Cl_2 needed to make 100 g of CCl_4 ($M_r = 154.0$) by $\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}$.

Problem 16 Tertiary halogenoalkane (hard)

For 2-bromo-2-methylpropane with aqueous hydroxide: $[\text{RBr}]$ 0.10, $[\text{OH}^-]$ 0.10, rate 3.0×10^{-5} ; $[\text{RBr}]$ 0.20, $[\text{OH}^-]$ 0.10, rate 6.0×10^{-5} ; $[\text{RBr}]$ 0.10, $[\text{OH}^-]$ 0.40, rate 3.0×10^{-5} (mol dm^{-3} and $\text{mol dm}^{-3} \text{ s}^{-1}$).

1. Deduce the rate equation and calculate k .
2. Calculate the half-life.
3. Explain why the carbocation intermediate is favourable.

Problem 17 Stereochemistry and profiles (hard)



Energy profiles for the two mechanisms.

Profiles A and B show hydrolysis of a halogenoalkane by SN_1 and SN_2 .

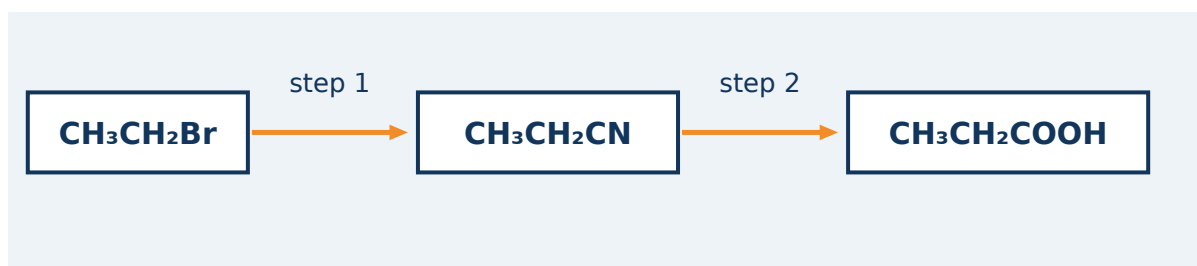
1. Identify which profile is SN_1 and explain.
2. An optically active secondary bromoalkane reacts by SN_2 ; describe the optical activity of the product.
3. Explain why optically active 3-bromo-3-methylhexane gives an optically inactive product by SN_1 .

Problem 18 Enthalpy of chlorination (hard)

Bond enthalpies (kJ mol^{-1}): C-H 413, Cl-Cl 242, H-Cl 432, C-Cl 346.

1. Calculate ΔH for $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$.
2. Calculate ΔH for each propagation step.
3. Explain why one photon can lead to thousands of product molecules.

Problem 19 Two-step synthesis (hard)



A two-step route from bromoethane.

Mei in Singapore plans to convert bromoethane into propanoic acid.

1. Give the reagent and conditions for each step.
2. Explain why ethanol is used in step 1.
3. Write the balanced equation for step 2 with hydrochloric acid and water.

Problem 20 CFCs and HFCs (hard)

A CFC is CFCl_3 . An HFC replacement contains C-F and C-H bonds but no chlorine.

1. Calculate the percentage of chlorine by mass in CFCl_3 (A_r : C 12.0, F 19.0, Cl 35.5).
2. Calculate the longest wavelength that can break a C-F bond (467 kJ mol^{-1} ; use $h = 6.63 \times 10^{-34} \text{ J s}$, $c = 3.00 \times 10^8 \text{ m s}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$).
3. Explain why HFCs damage ozone less.