A-LEVEL CHEMISTRY • EXERCISE SHEET

34.2 Phenylamine and azo compounds

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS phenylamine 苯胺 • azo compound 偶氮化合物 • phenylamine and azo compounds 苯胺与偶氮化合物 • phenol 苯酚 • dye 染料

Objective

Build the skills to answer exam questions on **phenylamine and azo compounds** 苯胺与偶氮化合物 — making phenylamine, diazonium salts, and azo dye coupling.

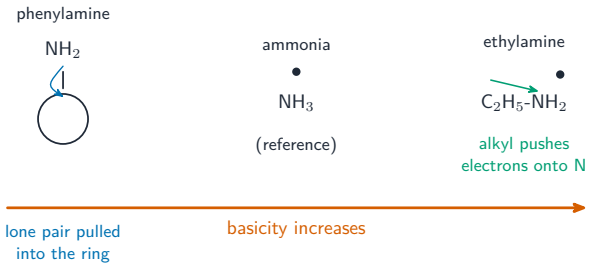
You must be able to:

- give the two-step route from benzene to phenylamine
- describe the formation of a diazonium salt and its conditions
- describe azo coupling and why azo compounds are coloured dyes

1 Worked examples

■ Diazonium salts and azo dyes

The strong colour of an azo dye comes from the –N=N– azo group joining two aromatic rings



Phenylamine is a weaker base than aliphatic amines

- **make phenylamine:** benzene → (nitrate) → nitrobenzene → (Sn / conc. HCl, then NaOH) → phenylamine.
- **diazonium salt:** phenylamine + $NaNO_2$ + dilute acid, **below 10 °C** → benzenediazonium chloride.
- **azo coupling:** diazonium salt + phenol in NaOH(aq) → a coloured **azo compound** (a dye); the –N=N– group links two rings.

■ Benzene to an azo dye, in three named steps

Step 1 — nitration. $C_6H_6 \rightarrow C_6H_5NO_2$ with concentrated HNO_3 and concentrated H_2SO_4 at 55 °C.

Step 2 — reduction to phenylamine 苯胺. $C_6H_5NO_2 \rightarrow C_6H_5NH_2$ with **tin and concentrated hydrochloric acid**, then **excess NaOH** to liberate the free amine from its salt. Both halves are marks; stopping at the tin/HCl step leaves you with the ammonium salt, not the amine.

Step 3 — diazotisation. $NaNO_2$ with dilute acid (which makes HNO_2 in situ) at **below 10 °C**, giving the **diazonium salt** 重氮盐 $C_6H_5N_2^+Cl^-$. The temperature is the mark: above about 10 °C the diazonium ion decomposes to phenol and nitrogen gas.

Step 4 — coupling. The diazonium salt is added to an alkaline solution of **phenol** (or another activated ring) to give an **azo compound** 偶氮化合物, an intensely coloured solid.

Why azo dyes are coloured. The two rings are joined through the $-N=N-$ **azo group**, which extends the **delocalised** system across the whole molecule. A larger delocalised system means a **smaller** energy gap between the levels, so the molecule absorbs light in the **visible** region, and the colour seen is the complement of what is absorbed. Changing the groups attached to the rings changes the gap, which is how a dye's colour is tuned.

Phenylamine is a weaker base than ethylamine — a favourite comparison. The nitrogen's lone pair is **delocalised into the benzene ring**, so it is less available to accept a proton. In ethylamine the alkyl group is electron-releasing and pushes

electron density onto the nitrogen, making the lone pair more available. Order: ethylamine > ammonia > phenylamine.

2 Practice

2.1 Give the reagents to reduce nitrobenzene to phenylamine. [2]

2.2 State the temperature needed to make a stable diazonium salt. [1]

2.3 Give the reagents and conditions for converting nitrobenzene into phenylamine. [3]

2.4 State why the diazotisation must be carried out below 10 °C. [2]

2.5 Explain why phenylamine is a weaker base than ethylamine. [3]

3 Exam-style questions

3.1 A diazonium salt is made from phenylamine using: [1]

- **A** $NaNO_2$ + dilute acid, below 10 °C
- **B** conc. HNO_3 + conc. H_2SO_4
- **C** Br_2 water
- **D** $LiAlH_4$

3.2 The colour of an azo dye is due to the: [1]

- **A** –OH group
- **B** $–NH_2$ group
- **C** –N=N– group
- **D** benzene ring alone

3.3 Outline the two-step synthesis of phenylamine from benzene, giving the reagents for each step. [3]

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(a) State the type of compound formed. [1]

(b) State **one** common use of such compounds. [1]

3.5 An azo dye is made from benzene in four steps.

(a) Give the reagents and conditions for step 1, the conversion of benzene into nitrobenzene, and name the mechanism. [3]

(b) Give the reagents for step 2 and explain why a second reagent is needed after the reduction. [3]

(c) Give the reagents and conditions for the formation of the diazonium salt, and write its formula. [3]

(d) The diazonium salt is coupled with phenol in alkaline solution. Draw the structure of the azo compound formed. [2]

(e) Explain, in terms of electrons, why azo compounds are coloured. [3]

Solutions

2.1 tin (Sn) and concentrated hydrochloric acid; then NaOH(aq).

2.2 below 10 °C (kept cold in an ice bath).

2.3 Tin and concentrated hydrochloric acid; then an excess of sodium hydroxide; heat under reflux.

2.4 Above about 10 °C the diazonium ion is unstable and decomposes to phenol and nitrogen gas, so the yield is lost.

2.5 In phenylamine the nitrogen's lone pair is delocalised into the benzene ring, so it is less available to accept a proton; in ethylamine the alkyl group releases electron density towards the nitrogen, making the lone pair more available.

3.1 A. $NaNO_2$ + dilute acid below 10 °C makes the diazonium salt.

3.2 C. The –N=N– azo group is responsible for the colour.

3.3 nitrate benzene with conc. HNO_3 + conc. H_2SO_4 to give nitrobenzene; reduce with Sn and conc. HCl; then add NaOH(aq) to free the phenylamine.

3.4 (a) an azo compound / azo dye.
(b) used as a dye (colouring).

3.5 (a) Concentrated nitric acid and concentrated sulfuric acid at about 55 °C; electrophilic substitution.
(b) Tin and concentrated hydrochloric acid; the product of the reduction is the phenylammonium salt, not the free amine, so excess sodium hydroxide is added to liberate phenylamine from it.
(c) Sodium nitrite with dilute hydrochloric acid, below 10 °C; $C_6H_5N_2^+Cl^-$.
(d) Two benzene rings joined by $-N=N-$, with the $-OH$ group para to the azo link on the phenol ring.
(e) The azo group $-N=N-$ joins the two rings into one extended delocalised system; a larger delocalised system has a smaller gap between the energy levels; the gap now corresponds to visible light, which is absorbed, and the complementary colour is seen.