

Concept QuickStart – Chemical Reactions of Amines

Unit 9: Amines

Subject: For CBSE Class 12 Chemistry

SECTION 1: UNDERSTANDING THE CONCEPT

Mastering the chemical reactions of amines is a strategic milestone in organic chemistry. The nitrogen atom in an amine is not just a placeholder; it is the "engine" of reactivity. This reactivity is almost entirely driven by the lone pair of electrons residing on the nitrogen atom. Because of this unshared pair, amines function as powerful nucleophiles and Lewis bases, seeking out electron-deficient centers to form new bonds. Understanding how this lone pair interacts with different reagents is the master key to organic synthesis, allowing chemists to bridge the gap between simple hydrocarbons and complex, functional molecules like amides or diazonium salts.

1.1 What Is the Reactivity of Amines? (Core Idea and Anchor Definition)

At the simplest level, imagine the nitrogen atom as a powerful "electronic magnet." While the carbon and hydrogen branches provide the shape of the molecule, the lone pair of electrons is the active tool that allows the amine to "grab" other atoms. Imagine this lone pair as a pair of hands reaching out to catch a passing proton or to attack a positive center in another molecule.

At the particle level, the nitrogen atom in amines is sp^3 hybridised. Three of these hybridised orbitals overlap with carbon or hydrogen, while the fourth orbital houses the lone pair. This lone pair creates a region of high electron density, making the nitrogen atom a nucleophilic center ready to donate its electron pair to electrophiles.

Anchor Definition: Amines are derivatives of ammonia obtained by the replacement of one, two, or all three hydrogen atoms by alkyl and/or aryl groups, characterised by a trivalent nitrogen atom carrying an unshared pair of electrons.

Correction of a Common Misunderstanding: Students often confuse basicity with acidity in this unit. Remember: Amines are Lewis bases because they donate their lone pair. They react with acids to form salts (like $R-NH_3^+Cl^-$), but they do not typically act as acids by losing protons under normal conditions.

1.2 Why Amine Reactions Matter

We care about these reactions because they are the foundation of life and industry. Biologically, amines are found in proteins, vitamins, and hormones like adrenaline. Industrially, they are used to synthesize polymers, dyes, and drugs. For example, Novocain (an anesthetic) and Benadryl (an antihistamine) rely on their amino groups for their medicinal

effects. In your CBSE exams, this unit is vital because it contains high-frequency "Name Reactions" that are the favorites of paper setters for conversion and identification questions.

1.3 Why This Concept Exists

The study of amine reactions exists to solve a specific problem: how to transform simple nitrogen compounds into complex materials. We use these reactions to build "chemical bridges." For instance, we can convert amines into diazonium salts, which are incredibly versatile intermediates used to create aryl fluorides, iodides, and vibrant azo dyes that cannot be made through direct substitution.

1.4 Analogies and Mental Image

Primary Analogy: Think of the nitrogen lone pair as a "magnetic hook." While the rest of the amine molecule provides the structure (like the body of a crane), the lone pair is the active hook that can grab onto electron-poor "cargo."

- **The Nitrogen Atom:** The central crane body.
- **The Lone Pair:** The magnetic hook looking for a target.
- **The Attacking Proton (H⁺):** The cargo being picked up to form a salt.

Mental Image: Picture this... Imagine a small, three-legged stool where the seat is the nitrogen atom and the three legs are the alkyl groups. Floating just above the seat is a glowing cloud—the lone pair. In a molecule like trimethylamine, the legs are pushed together so that the angle between them is exactly 108 degrees (slightly less than the standard 109.5 degrees). When a reaction occurs, you see this cloud "reach out" to pull in a positive particle, momentarily changing the stool's geometry.

This is what the chemical reaction of an amine looks like in your mind's eye.

1.5 Everyday Context and Applications

Observable Phenomenon: In the lab, lower aliphatic amines are easily identified by their "fishy" odor. If you add bromine water to aniline, you will see an immediate white precipitate of 2,4,6-tribromoaniline forming, which is a visual testament to how strongly the -NH₂ group activates the benzene ring.

Technology Application: Quaternary ammonium salts (R₄N⁺Cl⁻) are used as surfactants in fabric softeners and disinfectants. Because the nitrogen carries a permanent positive charge, one end of the molecule stays dissolved in water while the long carbon chains "stick" to oils and dirt, allowing them to be washed away.

Counterintuitive Example: You might think that more alkyl groups always make an amine more basic. While this is true in the gaseous phase ($3^\circ > 2^\circ > 1^\circ$), it is false in water due to "solvation" and "steric" effects. For your exam, memorize these specific aqueous basicity sequences:

- **Ethylamines:** $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
- **Methylamines:** $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$

Now that we've captured the "soul" of the reaction, let's look at the "skeleton"—the exact facts the examiners expect to see on your answer sheet.

SECTION 2: WHAT THE TEXTBOOK SAYS (NCERT)

When moving from conceptual understanding to exam preparation, precision is non-negotiable. While Section 1 helps you visualize the "why," this section focuses on the "what"—the specific facts and diagnostic tests required by the CBSE marking scheme.

2.1 NCERT Key Statements

- Amines behave as Lewis bases and nucleophiles due to the unshared electron pair on nitrogen.
- Basic strength is measured by pK_b ; a smaller pK_b value indicates a stronger base (e.g., Aliphatic amines pK_b 3.0–4.22 vs. Ammonia pK_b 4.75).
- Aliphatic amines are stronger bases than ammonia because alkyl groups (+I effect) increase electron density on the nitrogen.
- Aromatic amines (Aniline, pK_b 9.38) are weaker bases than ammonia because the lone pair is "delocalized" (shared) with the benzene ring, making it less available for protons.
- The Carbylamine Reaction is a test only for primary (1°) amines; it produces a foul-smelling isocyanide ($\text{R}-\text{NC}$) when heated with CHCl_3 and KOH .
- The Hinsberg Test uses Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) to distinguish 1° , 2° , and 3° amines based on the solubility of the resulting sulphonamide in alkali.

2.2 NCERT Examples and Distinctions

- **Diagnostic Example (Bromination):** Aniline is so reactive that it forms 2,4,6-tribromoaniline with bromine water. To get a single substitution, we must "protect" the amino group by reacting it with acetic anhydride to form **Acetanilide**. This reduces the nitrogen's activating power through resonance.
- **The Hinsberg Logic:**
 - **Primary Amines:** Form a sulphonamide that is **soluble in alkali** because it still has an acidic hydrogen atom attached to the nitrogen.
 - **Secondary Amines:** Form a product that is **insoluble in alkali** because there is no hydrogen atom left on the nitrogen.

- **Tertiary Amines:** Do not react with the reagent at all.

Bridging these textbook facts, Section 3 provides strategic anchors to ensure this information stays with you during the exam.

SECTION 3: CLARITY AND MEMORY

The biggest challenge in the Amines unit is keeping the "Name Reactions" and trends organized. Strategic memory anchors are essential to prevent confusion during high-pressure exam moments.

3.1 Key Clarity Lines

- **Rule 1:** Aniline is ortho-para directing, but direct nitration yields a significant amount of "meta" product because the acidic medium creates the anilinium ion ($C_6H_5NH_3^+$).
- **Rule 2:** Friedel-Crafts reactions (alkylation/acylation) fail with aniline because it reacts with the $AlCl_3$ catalyst to form a salt.
- **Rule 3:** Gabriel Phthalimide synthesis is the gold standard for pure primary aliphatic amines, but it cannot make aromatic amines (aniline) because aryl halides won't react with the phthalimide ion.
- **Rule 4:** Secondary and Tertiary amines are "Carbylamine Silent"—only 1° amines create the "foul smell."

3.2 How to Remember These Reactions

Mnemonic for Gabriel Phthalimide Synthesis: "Please Stop Adding Hydrogen"

- **P:** Phthalimide (Starting material)
- **S:** Salt formation (using KOH)
- **A:** Alkylation (adding R-X)
- **H:** Hydrolysis (releases the 1° Amine)

Mnemonic for the Hinsberg Test: "Primary Soluble, Secondary Insoluble, Tertiary None."
(Think: **PS-SI-TN**)

Memorable Phrase: "Hoffmann Bromamide **cuts the carbon.**" Use this to remember that the product amine always has one less carbon atom than the starting amide.

Physical Gesture: To remember the **Pyramidal Shape**, hold your hand out with three fingers pointing down (the R groups) and your thumb pointing slightly up (the lone pair). Imagine pushing the "legs" together until the angle is **108 degrees**. This "tripod" shape helps you visualize why amines are reactive at the top (the thumb/lone pair).

Extreme Association: *Get this wrong and you'll miss the smell!* Associate the **Carbylamine Reaction** with the most "foul, unbearable, rotten" smell imaginable. If an exam question mentions a "foul-smelling substance" (Isocyanide), your mind should immediately snap to the 1° Amine test.

By combining these conceptual models, textbook facts, and memory anchors, you now have the complete toolkit to master the chemical reactions of amines and excel in your examination.



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