ANILINE

Introduction and chemical properties of Aniline

Introduction

Aniline, an organic base integral in the production of various substances such as dyes, explosives, plastics, pharmaceuticals, rubber, and photographic chemicals, belongs to the class of organic compounds known as aminobenzene or phenylamine. These compounds, classified as aromatic amines, hold significance in numerous industrial processes while embodying the characteristics typical of aromatic compounds. Structurally, aniline compounds exhibit the formula $C_6H_5NH_2$, where the amino group is bound to the phenyl group.

In its natural state, aniline manifests as a yellowish to slightly brownish oily liquid, characterized by a distinctive fishy and musty odor reminiscent of rotten fish. This chemical substance, being a flammable liquid, emits an unpleasant odor. Aniline is soluble in water, presenting as a colorless to light brown solution. Its chemical composition, denoted by the formula $C_6H_5NH_2$ or C_6H_7N, signifies its organic nature, consisting of six carbon atoms, seven hydrogen atoms, and one nitrogen atom.

Chemical properties of Aniline

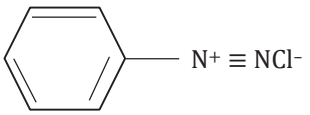
Aniline, with its chemical formula $C_6H_5NH_2$, exhibits several notable chemical properties:

- **Basicity:** Aniline is a weak base due to the presence of the amino group ($-NH_2$). It can undergo protonation reactions, where the lone pair of electrons on the nitrogen atom accepts a proton ($H+$), forming the anilinism ion ($C_6H_5NH_{3+}$).
- **Aromaticity:** Aniline is an aromatic compound, possessing a benzene ring (C_6H_5) attached to the amino group. This aromaticity influences its reactivity, often leading to electrophilic aromatic substitution reactions.
- **Acidity of the Aromatic Hydrogen:** The hydrogen atom attached to the benzene ring in aniline is slightly acidic compared to typical aliphatic hydrogens due to resonance stabilization of the resulting anion.
- **Substitution Reactions:** Aniline undergoes various substitution reactions typical of aromatic compounds. These include nitration, sulfonation, halogenation, and Friedel-Crafts acylation/alkylation.
- **Diazotization:** Aniline can be diazotized by treatment with nitrous acid (HNO_2) in acidic conditions, leading to the formation of diazonium salts. These salts are versatile intermediates in organic synthesis.
- **Oxidation:** Aniline can be oxidized to form various products depending on the conditions. Mild oxidation may lead to the formation of azoxy compounds, while strong oxidation can yield azo compounds, nitro compounds, or even quinones.
- **Polymerization:** Aniline can undergo polymerization reactions to form polyaniline, a conducting polymer with applications in electronics and sensors.

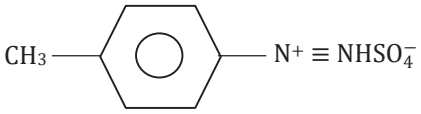
Formation of Diazonium Salt

Diazonium Salt

Diazonium salts can be denoted by the general chemical formula $ArN_2^+X^-$, where X– represents an anion, such as Cl^-, NO_3^-, BF_4^-, Br^-, HSO_4^-, among others. The positively charged N_2^- group within the structure is identified as the diazonium group, characterized by the nitrogen atoms doubly bonded to each other (N≡N). This distinctive diazonium group is pivotal in the chemical reactivity and behavior of diazonium salts.



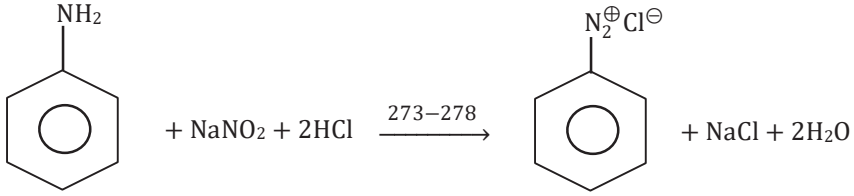
Benzimidazolium chloride



P–Toluene diazonium hydrogen sulphate

Methods of Preparation of Diazonium Salt

Benzene diazonium chloride is synthesized through the reaction of aniline with nitrous acid under controlled temperature conditions ranging from 273 K to 278 K. Nitrous acid, crucial for this reaction, is generated within the reaction mixture by the combination of sodium nitrite with hydrochloric acid. This process, commonly referred to as diazotization, entails the conversion of primary aromatic amines into diazonium salts. It's noteworthy that due to their inherent instability, diazonium salts are typically not stored but rather utilized promptly following their preparation.



Physical Properties

Benzene diazonium chloride exists as colorless crystalline solids with a high solubility in water. It exhibits stability when dissolved in cold water but undergoes reaction with water upon heating. However, in its dry state, it tends to decompose readily.

Chemical Reactions

Chemical reactions involving diazonium salts are diverse and versatile, allowing for the synthesis of various organic compounds. Some of the prominent reactions of diazonium salts include:

- **Coupling Reactions (Azo Dye Formation):** Diazonium salts can undergo coupling reactions with aromatic compounds, such as phenols or aromatic amines, to form azo compounds. This process, known as diazo coupling, involves the formation of a new carbon-nitrogen double bond between the diazonium salt and the coupling partner. Azo dyes, widely used in industries such as textiles and printing, are important products of diazo coupling reactions.
- **Sandmeyer Reaction:** In the Sandmeyer reaction, diazonium salts react with copper(I) salts to form aryl halides, aryl cyanides, or aryl thiols.
  For instance, in the presence of copper(I) chloride (CuCl), a diazonium salt can be converted into an aryl chloride:
  $$ArN_2^+X^- + CuCl \rightarrow ArCl + N_2 + Cu^+X^-$$
  This reaction is valuable for synthesizing various functionalized aromatic compounds.
- **Replacement Reactions:** Diazonium salts can undergo replacement reactions with different nucleophiles, leading to the introduction of new functional groups.
  For example, they can react with alcohols to form aryl ethers or with cyanide ions to form aryl nitriles.
- **Diazo Transfer Reactions:** Diazonium salts can participate in diazo transfer reactions, where the diazonium group is transferred to another molecule. For instance, in the Gattermann reaction, diazonium salts react with cuprous chloride (CuCl) to form diazonium chlorides, which can then react with aromatic compounds to introduce functional groups such as formyl (–CHO).

- **Electrophilic Aromatic Substitution:** Diazonium salts can undergo electrophilic aromatic substitution reactions, where the diazonium group acts as an electrophile. This reaction can lead to the introduction of various functional groups onto aromatic rings.
  These reactions highlight the versatility of diazonium salts in organic synthesis and their significance in the preparation of a wide range of organic compounds.