- 1° amine forms solid dialkyl oxamide $(CONHR)_2$
- 2° amine forms liquid dialkyl oxamlc ester$(CONR_2\text{-}COOC_2H_5)$
- 3° amlnes do not react

(c) Hlnsberg's method see.chemkal reactions.

**Benzene Diazonium Chloride** $(C_6H_5N_2^+;Cl^-)$

**Preparation** (Diazotisation reaction)

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5N{=}N{-}Cl + NaCl + 2H_2O$$

The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

**Properties**

It is a colourless crystalline solid, soluble in water. It has a tendency to explode when dry.

**Stability of Arenediazonium salts**

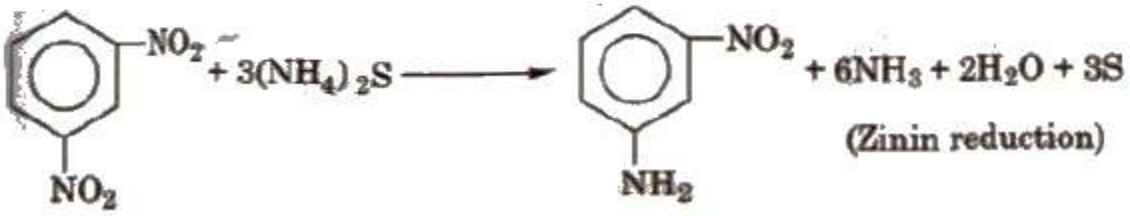
It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:

$$RNO_2 + 6[H] \xrightarrow{Sn/HCl} R—NH_2 + 2H_2O$$

If neutral reducing agent like Zn dust $+NH_4Cl$ is used, hydroxylamines are obtained as major product.

$$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} \underset{\text{N-alkylhydroxylamine}}{R—NHOH} + H_2O$$

In the presence of $(NH_4)_2S$ or $Na_2S$, selective reduction takes place.




Nitrobenzene gives different prociucts with different reagents and in different mediums.

| Medium | Reagent | Product |
|---|---|---|
| Acid | Sn/HCl | aniline |
| Neutral | $Zn/NH_4Cl$ | N-phenylhydroxylamine |
| | $Na_3AsO_3/NaOH$ | azoxybenzene ($C_6H_5N=\overset{O}{\uparrow}NC_6H_5$) |
| Alkaline | Zn/NaOH, $CH_3OH$ | azobenzene |
| | Zn/NaOH, $C_2H_5OH$ | hydrazobenzene |
| Metallic hydride | $LiAlH_4$ | aniline |
| Electrolytic | dil $H_2SO_4$ | *p*-aminophenol |



### (ii) Action of $HNO_2$

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

$$RCH_2NH_2 \xrightarrow[-H_2O]{HNO_2} \underset{\text{nitrolic acid}}{RC(NO_2)=NOH} \xrightarrow{NaOH} \underset{\text{(red)}}{RC(NO_2)=NONa}$$

2° nitroalkanes give pseudonitrol with $HNO_2$.

$$R_2CH(NO_2) \xrightarrow[-H_2O]{HNO_2} \underset{\text{pseudonitrol}}{R_2C(NO_2)—NO} \xrightarrow{NaOH} \text{Blue}$$