

PROPERTIES AND USES

PROPERTIES:

The mononitration of toluene results in the formation of a mixture of the ortho, meta, para isomers of nitrotoluene, $O_2NC_6H_4CH_3$. The presence of the methyl group on the aromatic ring facilitates the nitration, but it also increases the ease of oxidation.

(I) O-nitrotoluene:

O-Nitrotoluene is a clear yellow liquid. The solid is dimorphous and the melting points of the α and β forms are -9.55°C and -3.85°C respectively. O-Nitrotoluene is infinitely soluble in benzene, diethyl ether and ethanol. It is soluble in most organic solvents and only slightly soluble in water 0.065-gm/100 gm. of water at 30°C . The physical properties of o-Nitrotoluene are listed below:

Table - 2.1

| Property | Value | Property | Value |
|--|------------------|---|--------|
| Melting Point, $^\circ\text{C}$ α -form β - stable form | - 9.55 - 3.85 | Surface tension at 15 $^\circ\text{C}$ Dyne/cm | 42.3 |
| Boiling point, $^\circ\text{C}$ At 101 Kpa At 0.13 Kpa | 221.7 50 | Viscosity, CP, at 15 $^\circ\text{C}$ | 0.0262 |
| Density, gm/c.c ρ at 15 $^\circ\text{C}$ | 1.1622 | Heat of combustion at constant volume/MJ/mol ^b | 3.75 |
| Refractive index N | 1.5474 | Vapor density (Air =1) | 4.72 |

Chemical Properties:

1. Oxidation: The strong electron acceptor action of the nitro group in o-Nitrotoluene confers increased reactivity on the – CH₃ group; thus the methyl group is easily oxidized.

- Oxidation with Potassium permanganate or dichromate causes the formation of o-Nitro benzoic acid.
- When boiled with a sodium hydroxide solution, o-Nitrotoluene exhibits the phenomena of auto oxidation and reduction and yields anthranilic acid.
- When the oxidation is carried out with manganese dioxide and sulfuric acid, o-Nitro benzoic acid or o-Nitrobenzaldehyde is formed, depending on reaction conditions.

2. Reduction: o-Nitrotoluene is reduced to o-toluidine by iron powder and HCl acid.

- Alkaline reduction with Fe or Zn leads in a stepwise fashion to azoxy, azo and hydrazo compounds depending upon the reaction conditions.

3. Nitration:

Nitration of o-Nitrotoluene yields o-Nitrobenzyl chloride, o-chlorotoluene or o-chlorobenzyl chloride depending on the reaction conditions and in absence of iron.

In the presence of Fe, chlorination results in the formation of 2-nitro, 6-chloro toluene and 2-nitro, 4-chlorotoluene.

(II) **m-Nitrotoluene:**

m-Nitrotoluene is a clear, yellow liquid that freezes at 16.1⁰c. It is readily soluble in ethanol, benzene, and diethyl ether. It is soluble in most organic solvents and is sparingly soluble in water, 0.05-gm./100 gm. of water at 30⁰c. The properties of m-Nitrotoluene are listed below:

Table – 2.2

| <i>Property</i> | <i>Value</i> |
|--|-------------------------|
| Melting point, °C | 16.1 |
| Boiling point, °C (At 760 mm. Hg) | 231.9 |
| Density, Kg/m ³ | 1.16 x 10 ³ |
| Refractive index | 1.547 |
| Surface tension (at 30 ⁰ C), KN/mm. | 39.99 |
| Viscosity (at 30 ⁰ C), mPa.s (Cp) | 0.0178 |
| Heat of combustion (at constant volume), KJ/mol | 3.732 x 10 ³ |
| Vapour density (Air = 1) | 4.72 |
| Flash point (closed cup), °C | 106 |

Chemical properties:

1. Oxidation:

m-nitrotoluene does not have an active -CH₃ group as do the ortho- and para-isomers. It is oxidized readily to m-nitrobenzoic acid by chromic acid and more slowly by potassium hexacyanoferrate (III) in alkaline solution. M-nitrobenzaldehyde is the chief product of the electrolytic oxidation of m-nitrotoluene.

2. Reduction:

Acid, neutral or catalytic reduction of m-Nitrotoluene yields m-toluidine.

3. Nitration:

The nitration of m-nitrotoluene yields primarily 3,4 dinitro-toluene and small amounts of 2,3 dinitrotoluene and 2,5 – dinitrotoluene.

(III) **p-Nitrotoluene:**

p-nitrotoluene crystallizes in colorless rhombic crystals. It is only slightly soluble in water, 0.044gm/100gm. of water at 30⁰C; moderately soluble in methanol and ethanol. It is readily soluble in acetone, diethyl ether and benzene. The physical properties of p-Nitrotoluene are listed below:

Table – 2.3

| <i>Property</i> | <i>Value</i> |
|---|------------------------|
| Melting point, ⁰ c | 151.7 |
| Boling point, ⁰ c(At 760 mm. Hg) | 238.5 |
| Density, Kg/m ³ | 1.17 x 10 ³ |
| Refractive index | 1.5346 |
| Surface tension (at 60 ⁰ C), KN/mm. | 36.8 |
| Viscosity (at 60 ⁰ C), mPa.s (Cp) | 0.012 |
| Heat of combustion (at constant volume),KJ/mol | 3.72 x 10 ³ |
| Vapour density (Air = 1) | 4.72 |
| Flash point (closed cup), ⁰ C | 106 |

Chemical properties:

1. Oxidation:

The –CH₃ group of p-nitrotoluene is activated by the p-nitro group.

- P-Nitrotoluene is oxidized to p-nitrobenzoic acid potassium hexacynoferrate (III) in alkaline solution, potassium permanganate or dichromate.
- P-nitrotoluene is converted to p-nitro benzaldehyde by electrolytic oxidation in an acetic acid and sulfuric acid mixture or by treatment with lead (IV) oxide in concentrated H₂SO₄.

2. Reduction:

p-nitrotoluene is reduced by iron and hydrochloric acid to p-toluidine.

Alkaline reduction with Fe leads to the formation of a mixture of azoxy, azo and hydrazo compounds, depending upon reaction conditions.

3. Nitration:

Nitration of p-nitrotoluene yields 2,4, dinitrotoluene.

4. Chlorination:

The chlorination can occur on either the aromatic ring or the $-CH_3$ group, and the resulting product depends on the catalyst and reaction conditions.

- Under free radical reaction conditions, p-nitrobenzyl chloride is formed.
- In the presence of Fe or antimony (III) chloride, 4-nitro, 2-chloro-toluene is obtained.

5. Sulfonation:

p-Nitrotoluene yields 2-methyl, 5 nitrobenzene sulfonic acid on undergoing sulfonation.

6. Heating p-nitrotoluene with an alcoholic KOH solution results in the formation of 4,4- dinitrostilbene.

USES OF MONONITROTOLUENES:

Ortho nitrotoluene is used in the synthesis of intermediates for azo dyes, sulfur dyes, rubber chemicals and agricultural chemicals. Typical intermediates are o-toluidine, o-nitrobenzaldehyde, 2-amino, 4-chlorotoluene 2-nitro, 6-chloro toluene, 2-amino 4 chlorotoluene (fast scarlet TR base) and 2-amino 6-chlorotoluene (Fast red KB base);

Para nitrotoluene is used principally in the production of intermediates for azo and sulfur dyes. Typical; intermediate are p-toluene, p-nitrobenzaldehyde and 4-nitro 2 chlorotoluene.