

## PROPERTIES

### Physical Properties:

The physical and thermodynamic properties of toluene are summarized in Table 2.1. Vapor pressure data for toluene are summarized in Table 2.2. Toluene forms azeotropes with many hydrocarbons and most alcohols that boil in a similar range. All are minimum – boiling azeotropes.

As in benzene, the carbon – carbon bond lengths of the ring carbons in toluene are all the same length, 0.1397 nm, intermediate between normal single and double carbons in the benzene ring of toluene occupy three  $sp^2$  hybrid orbital and one  $2p_x$  orbital per carbon atom and one is electron per hydrogen atom. One  $sp^2$  electron of each adjacent carbon atoms to form a planar ring. The remaining six  $2p_x$  electrons combine to produce a  $\pi$  bond with a doughnut – shaped probability distribution on each side of the ring. These electrons are demoralized over the entire ring. This delocalization accounts for the stabilization energy of 163.2 kJ/mol (39 Kcal/mol) calculated from

*Table 2.1. Physical and thermodynamic Properties of Toluene*

| Property  | Value         |
|---|---------------|
| Mol wt  | 92.14         |
| Freezing pt, °C                                   | -94.965       |
| Boiling pt, °C                                    | 110.629       |
| Density , g/cm <sup>3</sup>                       |               |
| At 25 <sup>0</sup> C                              | 0.8623        |
| At 20 <sup>0</sup> C                              | 0.8667        |
| Critical properties                               |               |
| Temperature, °C                                   | 318.64        |
| Pressure, Mpa (atm)                               | 4.109(40.55)  |
| Volume, L/mol                                     | 0.316         |
| Heat of combustion, at 25 <sup>0</sup> C constant | 3910.3(934.5) |
| Pressure, kJ/mol(Kcal/mol)                        |               |
| Heat of vaporization, kJ/mol(kcal/mol)            |               |
| At 25 <sup>0</sup> C                              |               |

|   |                |                        |
|---|----------------|------------------------|
| At bp   |                | 37.99(9.080)           |
| Heat capacity, J/(g.K)(cal/g.K)                             |                | 33.18(7.931)           |
| Ideal gas   |                |                        |
| Liquid at 101.3kPa(1atm)                                    |                | 1.125(0.2688)          |
| Surface tension at 25 <sup>0</sup> C, mN/m<br>(=dyn/cm)     |                | 1.970(0.4709)<br>27.92 |
|   | Gas            | Liquid                 |
| heat of formation, $\Delta H^0_f$ , kJ/mol<br>(kcal/mol)    | 50.00 (11.950) | 12.00(2.867)           |
| entropy, S <sub>0</sub> , kJ/K (kcal/K)                     | 319.7 (76.42)  | 219.6(52.48)           |
| free energy of formation, $\Delta H^0_{f,kJ/K}$<br>(kcal/K) | 93.00 (22.228) | 114.1(27.282)          |

**Table 2.2, Vapor pressure of Toluene:**

| Temperature, °C | Prassure<br>KPa(mm Hg) | Temperature, °C | Prassure<br>KPa(mm Hg) |
|-----------------|------------------------|-----------------|------------------------|
| 0               | 0.91(6.8)              | 160             | 342.0(3,385)           |
| 20              | 2.92(21.9)             | 180             | 516.8(5,100)           |
| 40              | 7.91(59.3)             | 200             | 749.3(7,395)           |
| 60              | 18.56(139.2)           | 220             | 1053(10.30)            |
| 80              | 38.86(291.5)           | 240             | 1441(14.22)            |
| 100             | 71.19(556.5)           | 260             | 1927(19.02)            |
| 120             | 131.2(1,295)           | 280             | 2530(24.97)            |
| 140             | 217.8(2,150)           | 300             | 3273(32.30)            |

The observed heats of combustion compared to calculated heats of combustion for a cyclohexatriene – type structure with alternate and fixed single and double carbon bonds. The same value for stabilization energy is obtained from heats of hydrogenation.

### **Chemical Properties:**

Because of the high electron density in the aromatic ring, toluene behaves as a base both in formation of charge – transfer  $\pi$  complexes and in the formation complexes with super acids. In this regard, toluene is intermediate between benzene and the xylenes. In the formation of  $\pi$  complexes with electrophiles such as silver ion, hydrogen chloride, and tetracyanoethylene, toluene differs from either benzene or the xylenes by less than a factor of two in relative basicity. The difference is small because the complex is formed almost entirely with the  $\pi$  electrons of the aromatic ring; the inductive effect of the methyl group provides only minor enhancement. In contrast, with HF and BF<sub>3</sub> which form a sigma – type complex, or in the case of reaction as with nitronium ion or chlorine where formation of sigma bonds and complexes plays a predominant role, the methyl group participates by hyperconjugation and the relative reactivity of toluene is enhanced by several orders of magnitude compared to that of benzene. Reactivity of xylenes is enhanced again by several magnitudes over that of toluene. Thus, when only the  $\pi$  electrons are involved, toluene behaves much like benzene and the xylenes.

When sigma bonds are involved, toluene is a much stronger base than benzene and a much weaker base than the xylenes. The reasons for this difference are readily shown by contrasting the complexes of toluene with hydrogen chloride in the absence and presence of aluminum chloride. In the absence of aluminum chloride, hydrogen chloride is loosely attracted to the  $\pi$  cloud of electrons above and below the plane of the ring. With aluminum chloride present, the electrophilicity is greatly enhanced and a sigma bond is formed with a specific electron pair; structures involving the methyl group contribute to the stabilization.

For attack at either of the two ortho positions or the para position, three such structures can be written.

Chemical derivatives of toluene are formed by substitution of the hydrogen atoms of the methyl group, by substitution of the hydrogen atoms of the ring, and by addition to the double bonds of the ring. Toluene can also undergo a disproportionation reaction in which two molecules react to yield one molecule of benzene and one molecule of xylene.

**Substitutions on the methyl Group:** The reactions that give substitution on the methyl group are generally high temperature and free – radical reactions. Thus, chlorination at ca 100<sup>0</sup>C, or in the presence of ultraviolet light or other free – radical initiators, successively gives benzyl chloride, benzal chloride, and benzotrichloride.

With oxygen in the liquid phase and particularly in the presence of catalysts, eg. bromine – promoted cobalt and manganese, very good yields of benzoic acid are obtained.

In the presence of alkali metals such as potassium and sodium, toluene is alkylated on the methyl group to yield, successively, normal propylbenzene, 3 – phenylpentane, and 3 – ethyl – 3 – phenylpentane .

In the presence of a potassium catalyst dispersed on calcium oxide, toluene reacts with 1,3-butadiene to yield 5-phenyl-2-pentene.

When lithium is used as a catalyst in conjunction with a chelating compound such as tetramethylethylenediamine (TMEDA), telomers are generally obtained from toluene and ethylene.

The intermediates in these base-catalyzed reactions are believed to be of the nature of a benzyl cation because the reaction product from toluene and propylene is isobutylbenzene, not n-butylbenzene, and the reaction rate is slower than with ethylene.

**Addition to the Ring:** Additions to the double bonds in the aromatic ring of toluene result from both free-radical and catalytic reactions. Chlorination using free-radical initiators at temperatures  $<0^{\circ}\text{C}$  saturates the ring. However, this reaction is not entirely selective, for in addition to saturating the ring to yield hexachlorohexane derivatives, the reaction also effects substitution on the methyl group. Hydrogenation with typical hydrogenation catalysts readily yields methylcyclohexane. However, rates for

hydrogenation of toluene are only 60-70 % of that for benzene. The commercial technology used for hydrogenating benzene to cyclohexane can be directly applied to manufacture of methylcyclohexane. Both of these ring – saturating reactions probably proceed stepwise, but since the initial reaction must overcome the high resonance energy of the aromatic ring, saturation of the second and the third double bond is much more rapid with the result that partially saturated intermediates are not normally detected .

**Substitution on the Ring:** Substitution of the ring hydrogen atoms by electrophilic attack takes place with all of the same reagents that react with benzene. Some of the common groups with which toluene can be substituted directly are:

And  $\text{CH}_2\text{Cl}$ .

Generally, these increased reactivities of toluene and the related selectivity to the ortho and para positions can be explained in terms of the inductive effect of the methyl group, which increases the electron density in the ring, and by the ability of the methyl group to hyperconjugate (as shown below) and thereby stabilize the reaction intermediates.

In addition to these effects, there is a steric effect at the ortho position as shown by the data in Table 6. these data clearly demonstrate that bulky groups cannot enter easily into the position adjacent to the methyl group and therefore attack selectively at the para position.

Toluene itself does not undergo substitution by nucleophilic attack of anions but requires substitution by strongly electronegative groups, such as nitro groups, before the ring becomes sufficiently electrophilic to react with anions. Detailed treatment of aromatic electrophilic substitutions can be found in references 21 and 22.

**Miscellaneous Reactions:** Several other types of reactions of toluene are also used commercially or are of potential commercial interest and are discussed in more detail in Utilization and Potential Uses of Toluene. These are thermal hydrogenolysis to yield benzene, methane, and biphenyl;