The Hydroxylation of Toluene Using Cadmium Sulphide as a Photocatalyst

Rashmi Bhatia, Sonika Bahedia, Pinki B. Punjabi and Suresh C. Ameta

Department of Chemistry, College of Science
M.L. Sukhadia University, Udaipur-313002, India

The photocatalytic substitution reaction of toluene was studied. For this purpose, toluene was hydroxylated in the presence of semiconductor (CdS) and sodium hydroxide. The effect of different parameters like amount of NaOH and CdS, intensity of light, etc. on the rate of reaction was studied. On the basis of observed data, a tentative mechanism for the hydroxylation of toluene has been proposed.

The hydroxylation of toluene is a substitution reaction because toluene is an electron rich molecule and therefore, it is not easily attacked by a nucleophile under ordinary reaction conditions. It is of utmost importance to find out an alternate pathway for carrying out the hydroxylation of an aromatic system like toluene. For this purpose, the hydroxyl radicals may be generated in the aqueous medium by exposing the mixture of toluene and an aqueous solution of sodium hydroxide in the presence of light and semiconducting cadmium sulphide. These hydroxyl radicals then attack the toluene moiety and thus result in the formation of cresols. The main object of the paper is to determine the mechanism as well as improve the yield.

Experimental

A mixture of toluene, (20.0 mL), 1.0 x 10^{-2} M NaNH solution (50.0 mL), and Cds (Reidel) (0.14 g) was irradiated with a 200 W tungsten lamp. The intensity of light was kept 60.0 mWcm^{-2} as measured by a solarimeter (Surymapi CEL 201). A water filter was used to cut-off thermal radiations. The progress of reaction was studied spectrophotometrically by using phenolphthalein as an indicator. The optical densities of aliquots of the aqueous pink solution at different time intervals were measured at \(\lambda_{max} = 555\) nm using a Systronics 106 spectrophotometer. It was observed that within a few hours, the optical density of the solution decreased considerably; thus, indicating that sodium hydroxide was consumed in this process. The amount of cresols was also estimated spectrophotometrically (\(\lambda_{max} = 380\) nm) using 2.0 mL of ferric chloride (3.18 x 10^{-3} M) and the yield was 2.50%. Some control experiments were also carried out. It was observed that in these experiments, the reaction either proceeds very slowly or does not occur at all in the absence of a semiconductor.

*Corresponding author: ameta_cs@yahoo.com sonikabahedia@yahoo.com

Niiranen et al. studied the photosubstitution of naphthalene and phenanthrene with two nucleophiles (hydroxide and cyanide ions) in water - acetonitrile (1:1) in the presence and absence of p-dicyanobenzone. The hydroxylation of benzoic acid was reported by Sedlak et al., while the photochemical oxidation of benzene and N-alkylbenzene were also reported. There are some more reports on hydroxylation of vitamin D6 and cholesterol. Takizawa et al. observed chemical hydroxylation of phenols. Recently, hydroxylation of azulene has also been carried out by Makoszam and Podraza while Joseph et al. reported photochemical production of hydroxyl radicals. The hydroxylation of benzene using titanium dioxide as a semiconductor was studied by Bhatia et al.
Results and Discussion

The experimental data observed for a typical run for photocatalytic hydroxylation of toluene are given in Table 1 and graphically represented in Figure 1. These are based on three trials and the average has been reported. The plot of $1 + \log (\text{O.D.})$ vs time (hr.) was found to be a straight line; Thus, indicating that the reaction follows first order kinetics. Therefore, the rate constant ($k$) of the reaction was determined by the expression $k = 2.303 \times \text{slope}$. The value of the rate constant of this reaction was found to be $4.13 \times 10^{-5}$ sec$^{-1}$.

![Figure 2.1. Experimental set-up.](image)

### Effect of NaOH Concentration

The rate of the reaction may be affected by the variation of amount of NaOH. Different amounts of NaOH were used in different sets, keeping all other factors identical. The results are given in Figure 2.

It was observed that the rate of hydroxylation increases on increasing the concentration of sodium hydroxide. It reaches a maximum at $[\text{NaOH}] = 1.0 \times 10^{-2}$ M, above which, it starts decreasing. This variation may be explained on the basis that on increasing the concentration of sodium hydroxide, there is a corresponding increase in the concentration of hydroxyl ions and more IOH radicals are generated from these OH- ions by holes.

$$h^+ + \text{OH}^- \rightarrow \text{IOH}$$

However, if the concentration of hydroxyl ion was increased further above $1.0 \times 10^{-2}$ M, hydroxyl ions will be adsorbed on to the semiconductor surface giving it a negative charge. Now OH- ions in the bulk of the solution will face a columbic repulsion from the adsorbed OH- ions, and as a consequence, the rate of generation of hydroxyl radicals will decrease and in turn, a decrease in the rate of reaction has been observed.

### Effect of Amount of Semiconductor

The rate of reaction was also observed by varying the amount of CdS and keeping the amount of toluene and concentration of NaOH fixed. The results are summarized in Figure 3.

It is clear from the data given above graph that as the amount of CdS increases, the rate constant also increases but after a certain limit, a plateau was
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Figure 1. Photocatalytic hydroxylation of toluene.

Figure 2. Effect of NaOH concentration on rate constant.

Figure 3. Effect of amount of semiconductor on rate constant.
observed. This may be attributed to the fact that as the amount of semiconductor increases, the exposed surface area also increases but when amount of CdS was increased above 0.14 g, there is no increases in the exposed surface area of the photocatalyst. At this point, increase in semiconductor will only increase the thickness of the layer at the bottom of the vessel and not the exposed surface area and hence, the rate becomes constant.

Effect of Light Intensity

The results of the effect of light intensity on the rate of the reaction are reported in Figure 4.

It was observed that increase in light intensity increases the rate of the reaction because more photons are available for excitation of electrons in the conduction band leaving a hole in valence band, which ultimately leads to the formation of more OH radicals and hence, the reaction rate was accelerated.

Mechanism

On the basis of data and corroborating the existing references, the following tentative mechanism has been proposed for the photocatalytic hydroxylation of toluene.

SC, CB and VB represents semiconductor, Conduction Band and Valence Band, respectively.

The participation of hydroxyl radicals as an active oxidizing species in hydroxylation reaction was confirmed by using IOH radical scavengers like isopropanol, formate ions, etc. It was observed that the rate of reaction was drastically reduced in the presence of these scavengers.

\[
\text{HCOO}^- + \text{IOH} \quad \text{CO}_2 + \text{H}_2\text{O} \quad (6)
\]

It may be concluded that IOH radicals play an
important role in hydroxylation of aromatic moiety like toluene.

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References


