# CHAPTER III

AROMATIC SUBSTITTUTION

This chapter describes about the phenomenon of aromatic substitution, the factors affect to the substitution and previous works concerning hydroxylation of alkyl benzene.

3.1 Benzene substitution

An electrophile accepts an electron pair from the ¶ system to form carbonation showed in Figure 3.1, it is a resonance-stabilized one of allylic type. It is a cyclohexadineyl cation (often referred to arenium ion).


Benzene and electrophile   Carbocation
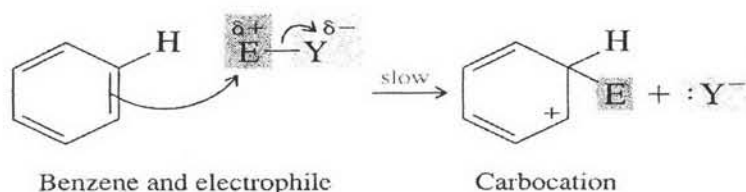
Figure 3.1 An electrophile accepts an electron pair from the ¶ system to form carbonation [4]

Most of the resonance stabilization of benzene is lost when it is converted to the cyclohexadineyl cation intermediate which is not aromatic and posses only a fraction of the resonance stabilization of benzene. Once formed, it rapidly loses a proton, restoring the aromaticity of the ring and the product of electrophilic aromatic substitution. The route of resonance stabilization of benzene conversion is illustrated in Figure 3.2
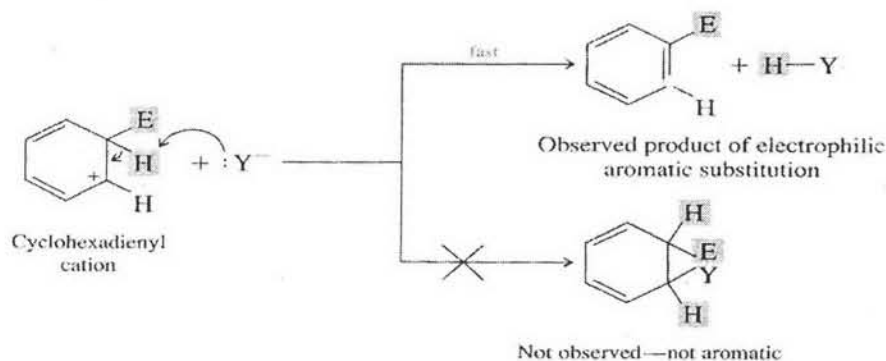
Figure 3.2 The resonance stabilization of benzene is converted to the cyclohexadineyl cation [4]

If the Lewis base (:Y) acted as a nucleophile and add to carbon, the product would have a nonaromatic cyclohexadiene derivative. Addition and substitution product arise by alternative reaction paths of a cyclohexadienyl cation. Substitution occurs preferential because a substantial driving force favors re-aromarization. The electrophilic aromatic substitution occurs in two steps. The first step forms cyclodienyl cation intermediate, represented by the energy minimum between the two maxima diagram. Each reaction step has energy maximum that is the transition state of that elementary step. The first substitution is slow step of the reaction, and its activation energy is higher than of the second step that are presented in Figure 3.3.
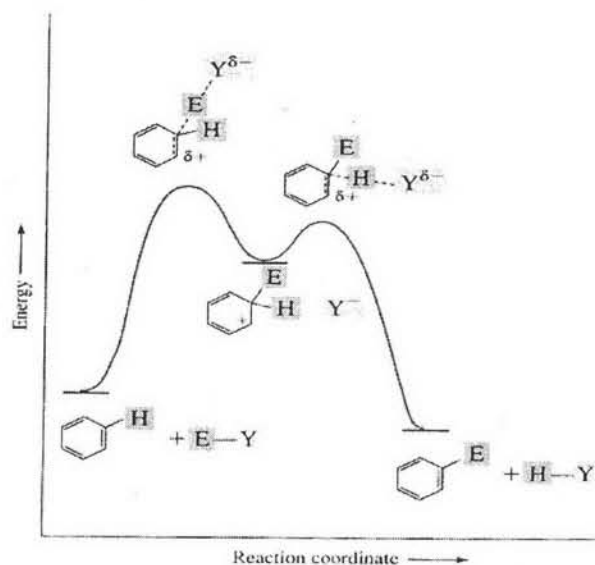

Figure 3.3 The electrophlic aromatic substitution occurs in two steps [4]
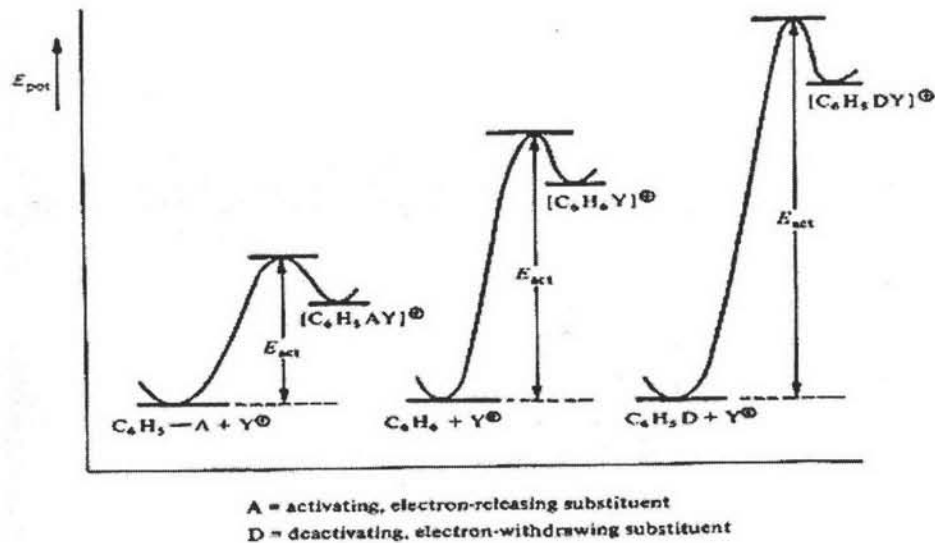
3.1.2 Effect of substitutions

When substituted benzene compounds undergo electrophilic substitution reactions of the kind discussed above, two related features must be considered:

I. The first is the relative reactivity of the compound compared with benzene itself. Experiments have shown that substitutes on a benzene ring can influence reactivity on it. For example, a hydroxy or methoxy substituent increases the rate of electrophilic substitution about ten thousand fold. In contrast, a nitro substituent decreases the reactivity ring by roughly a million. This activation or deactivation of the benzene ring toward electrophilic substitution may be correlated with the electron donating or electron withdrawing influence of the substituents, as measured by molecular dipole moments. For benzene molecule has a dipole moment of symmetry that equals zero. But mono-substituted benzenes have unsymmetrical electron density distributions. Electron-donating group increase the electron density of benzene nucleus making the nucleus more nucleophilic toward electrophile reagents. These groups activate aromatic ring system. Electron-withdrawing group decrease the electron density of the benzene nuclease making the nuclease less nucleophilic toward electrophile reagents. These groups deactivate the aromatic ring system. Electron-donating in the following Figure 3.4 that electron donating substituents activate the benzene ring toward electrophilic attack, and electron withdrawing substituents deactivate the ring (make it less reactive to electrophilic attack).

Activating Substituents

1.32   1.45   1.20   0.40

Deactivating Substituents


3.97   3.90   1.91   1.56
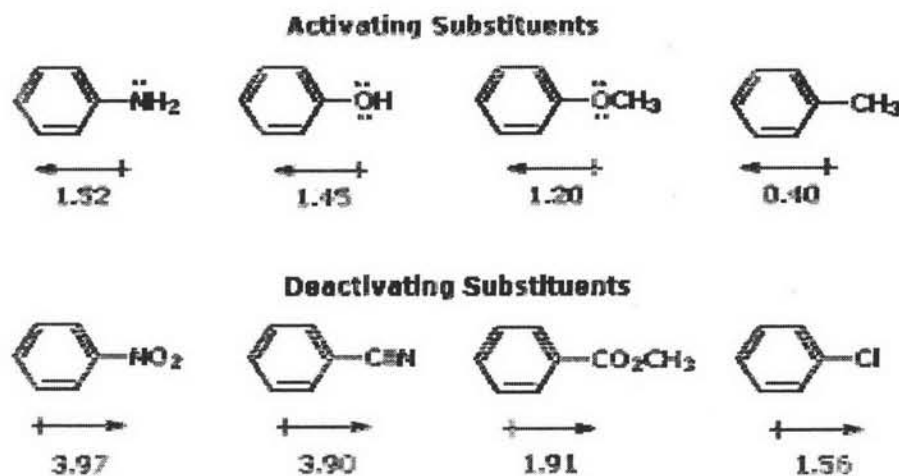
Figure 3.4 Diagram of the electron donating substituents and electron withdrawing substituents [4]

The substituent has effect to activation energy controlling the kinetic of reaction and showed in Figure 3.5. For, activating substituent or electron releasing effects decreases the activation energy and deactivating substituent or electron withdrawn effect increase the activation energy.


A = activating, electron-releasing substituent
D = deactivating, electron-withdrawing substituent

Figure 3.5 Effect of activation energy of substituent controls kinetic reaction[14]

II. An important in reactions of substituted benzenes concerns the site at which electrophilic substitution occurs. Since a mono-substituted benzene ring has two equivalent ortho-sites, two equivalent meta-sites and a unique para-site, three possible constitutional isomers may be formed in such a substitution that reveals in Figure 3.6.
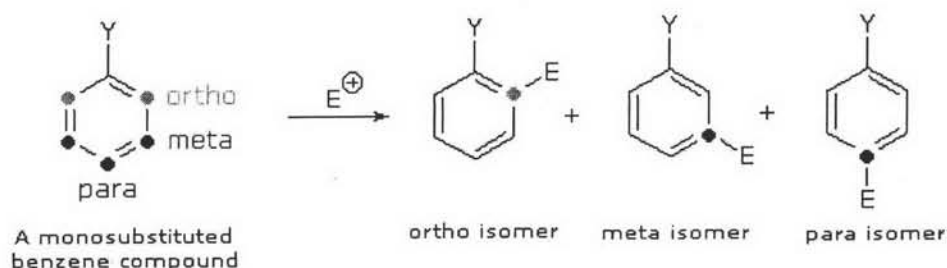
Figure 3.6 the site of electrophilic substitutes on benzene ring[4]

From Figure 3.7, for example, an activating substituent (CH_3) three resonance structures can be drawn for attack at each position (ortho, meta, para), (A.) ortho substitution, first structure is especially stable as positive charge located on carbon with electron releasing substituent help reduce charge, (B.) meta substitution no resonance structure can be drawn with positive charge on carbon bearing electron releasing substituent-less stable and (C.) para substitution, the resonance with positive charge on carbon bearing release substituent-extra stability [3,14].

A.

B.

C.
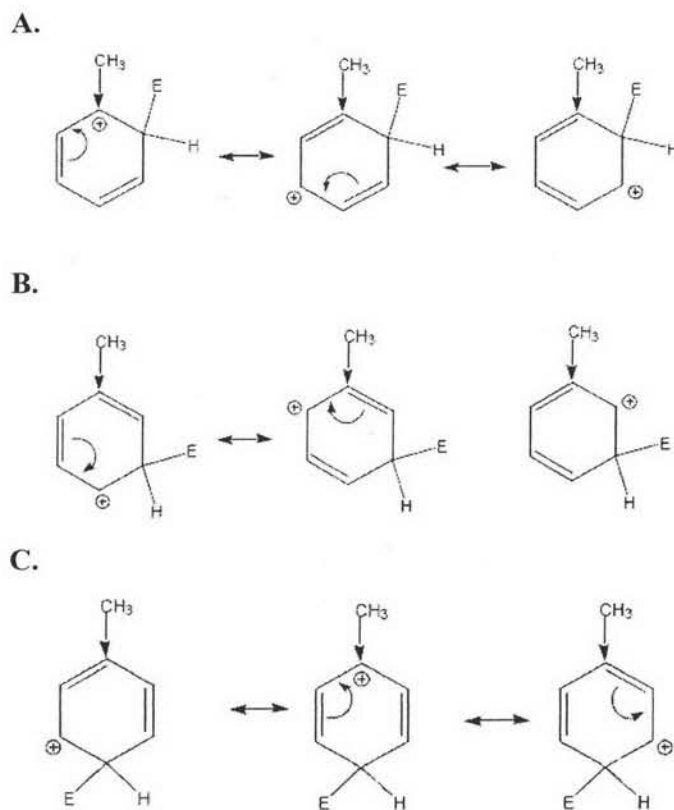
Figure 3.7 an activating substituent three resonance structures can be drawn for attack at ortho, meta and para[14]

3.2 Hydroxylation of aromatic hydrocarbon

In previous work, the effect of various reaction parameters on conversion and selectivity under triphase condition in the hydroxylation of aromatic hydrocarbon as benzene, toluene, p-xylene, ethylbenzene and anisole. Other, this work explored the reason of enhanced activity and p-selectivity in the hydroxylation of such aromatic compound under solvent free triphase condition.

3.2.1 Hydroxylation of benzene

The hydroxylations of benzene diagram are shown in Figure 3.8, phenol as catechol, hydroquinone and p-benzoquinone as by-product.
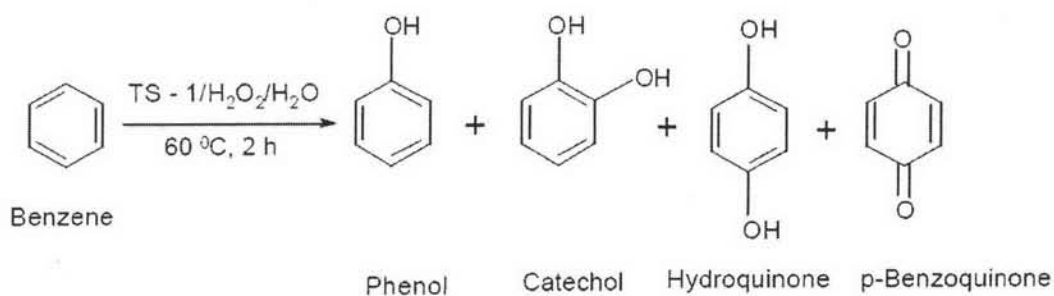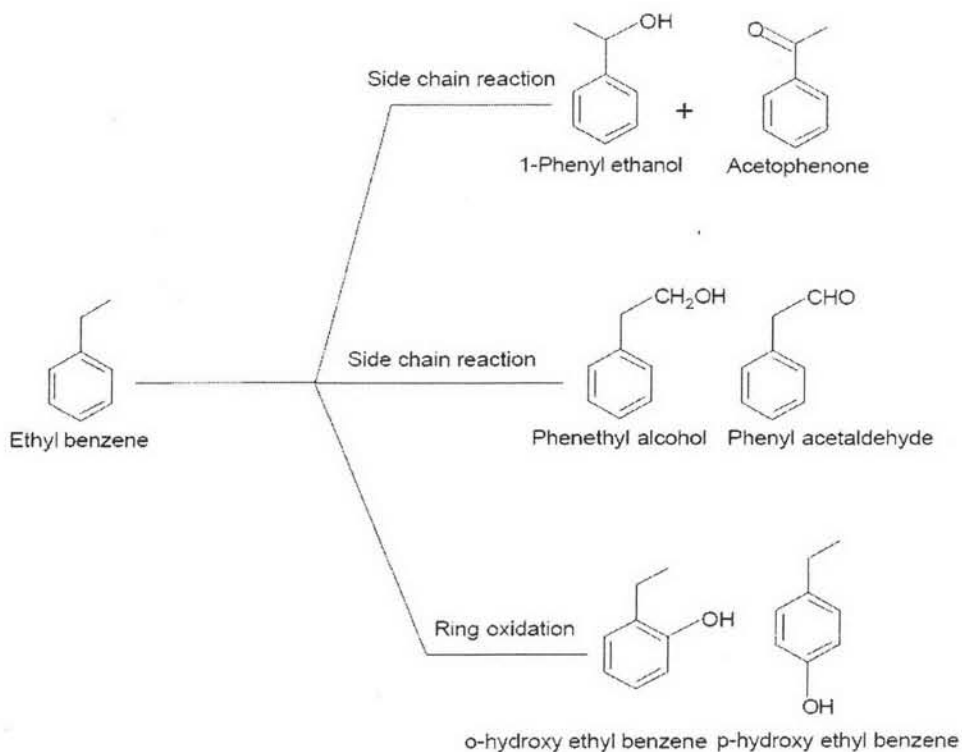

Figure 3.8 Hydroxylation of benzene over TS-1 catalyst [11]

The conversion of reactant was very low because introduction of hydroxyl group activates the aromatic nucleus to further oxidation to hydroquinone, catechol and p-benzoquinone (secondary oxidation product).

The rate of reaction under biphase was slower than triphase condition which found a reaction was very fast from to reach maximum conversion level. In case the total amount of H_2O_2 was added in one lot at the beginning of the reaction, it made the secondary products were formed because of increasing rate at the beginning. For H_2O_2 was added slowly at different interval of times. Here, phenol selectivity increased slightly with time at the initial stage of the reaction. Under triphase condition, it have optimum temperature at 60°C (phenol selectivity 85.6 % mole), so all other experiments were carried out at this temperature.

3.2.2 Hydroxylation of ethylbenzene

Figure 3.9 Hydroxylation of ethyl benzene over TS-1 catalyst[11]

Figure 3.9 presents the products obtained from hydroxylation of ethyl benzene. The reaction used water for triphase and co-solvent for biphase. The maximum conversion and H_2O_2 efficiency was observed in triphase and the minimum was observed in the case of co-solvent as acetonitrile. For ring oxidation was observed maximum in triphase and minimum in biphase. But in case of side chain, the reaction was maximum in biphase and minimum in triphase. Therefore, biphasic reaction is more susceptible to side chain oxidation than the triphasic one. It was further observed the ratio of secondary carbon oxidation to primary carbon oxidation was much more in case of biphase (acetone as co-solvent) that showed the secondary carbon was preferentially oxidized compared to primary one.

The effect of reaction time was observed the increasing ring oxidation product and decreasing side chain oxidation product, when increased the reaction time. The oxidation could take place in the ring or in the side chain because of the relatively larger size of the ethyl benzene that hindered to enter the pore of TS-1. Therefore, the reaction was predominantly dominated by surface reactive species. However, between the ring oxidation product was the p-isomer always predomination.

Effect of dilution on ethyl benzene hydroxylation was observed and shown the maximum ring oxidation product was obtained at optimum dilution level. The selectivity of ortho- and para-product change with diluted level and the amount of ortho- and para-product was less in lowest and highest dilution. The side chain reaction oxidation was much at minimum diluted level and the formation of secondary carbon oxidation products decreased with increasing diluted level.

The effects of different Ti content of TS-1 were studied. In case decreasing Ti-content of catalyst was observed H_2O_2 efficiency and the side chain oxidation decreased, on the other hand the ring oxidation increased. For the para-selectivity of product gradually increased with increasing in Si/Ti ratio of TS-1 and the secondary carbon oxidation increased with increasing Ti-content of the catalyst.

3.2.3 Hydroxylation of toluene
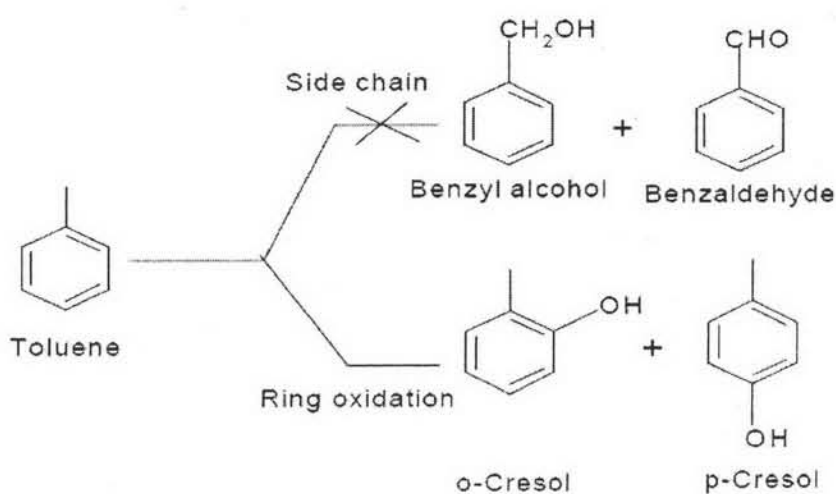
Figure 3.10 Hydroxylation of toluene over (TS-1) catalyst [11]

The products and rout of hydroxylation toluene are presented in Figure 3.10, it was obtained o-cresol and p-cresol from the ring oxidation.

Effect of stirring on catalytic hydroxylation of toluene in triphase was observed the conversion of p-cresol selectivity increase with increase of stirring speed but o-cresol selectivity decrease. Due to the increasing stirring rate effect to transportation of reactant to catalyst increase and diffused to inside pore. The reaction mainly occurred inside the relatively hydrophobic TS-1 channels resulting in increased conversion and p-cresol selectivity.

Effect of time was observed the reaction was fast at beginning. The increment of conversion and H_2O_2 efficiency with time was associated with progressive increasing p-selectivity.

Effect of toluene to H_2O_2 molar ratio was observed increasing this ratio, there was progressive increasing H_2O_2 efficiency as well as para-selectivity. At low ratio, the selectivity for para-cresol was less compared to that at higher molar ratio. The active species inside the pore might be mainly contributing catalytic site.

Effect of diluted level was observed the increasing dilution affected to H_2O_2 efficiency and para-cresol selectivity to increase.

Effects of different Ti content of TS-1 catalyst were studied. The results were observed the increasing Si/Ti ratio, there was a progressive increase in p-cresol, although, there was a decrease in H_2O_2 efficiency. This could be explained with the relatively hydrophobic behavior of different TS-1 species. It would increase with decreasing Ti-content in catalyst. The less the amount of Ti- would be the local polarization of Si-O-Ti bound and more hydrophobicity. The adsorption of the hydrophobic molecules inside the TS-1 channels leaded to the increase shape selective para product [11].