

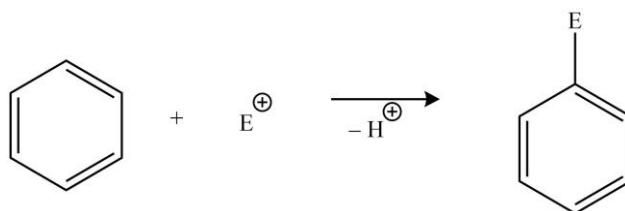
CHAPTER 8

Aromatic Electrophilic Substitution

❖ The Arenium Ion Mechanism

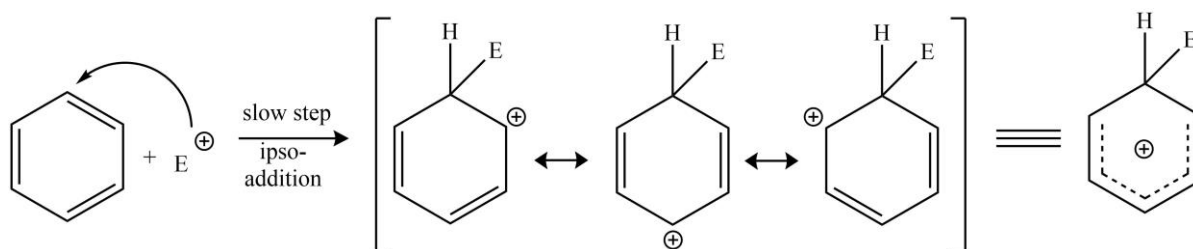
Electrophilic aromatic substitution (EAS) is the organic reaction in which an atom that is attached to an aromatic system (typically hydrogen) is replaced by an electrophile. This is quite possible in aromatic systems because there is π -electron density above and below the plane which is easily available for attacking electrophile; and nucleophilic attack is opposed because of π -cloud shields the carbon from such invasions.

Illustrative reaction: The general reaction showing the electrophilic substitution in aromatic compounds is shown below (E is electrophile).

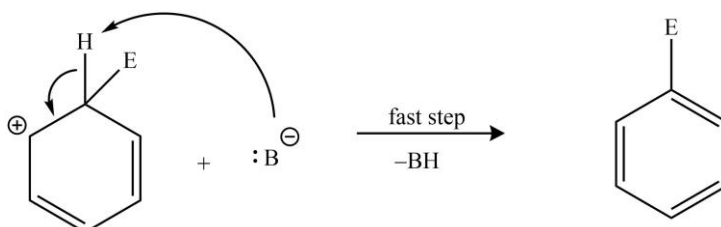


Mechanism involved: The proposed mechanism for the reaction given above involves three steps which must be discussed before we give salient features of the same.

i) *Attack of the electrophile on aromatic ring forming carbocation intermediate:* In this step, the electrophile attacks the aromatic ring to form a resonance stabilized carbocations.



iii) *Departure of the leaving group:* In this step, the leaving group detaches itself from the aromatic ring to give rise to the final product.



Salient Features: The main features of the mechanism involved in electrophilic aromatic substitution type reactions are given below.

i) The aromatic electrophilic substitution (EAS) reactions follow second-order kinetics with the rate law as give below.

$$\text{Rate} = k[\text{RX}][\text{E}]$$

Where k is the rate constant. The symbol $[\text{RX}]$ and $[\text{E}]$ represent the molar concentration of the substrate and attacking electrophiles, respectively.

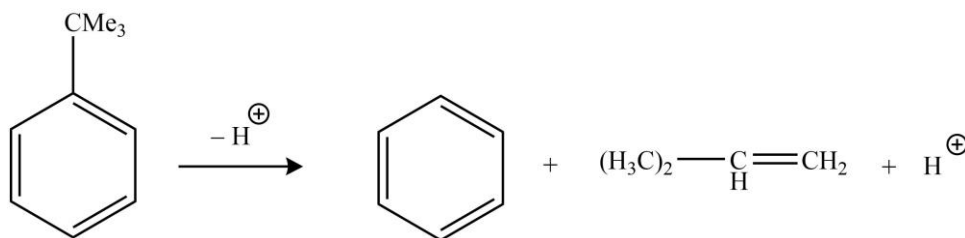
ii) The substituents like $-\text{XY}$, where X has lone pairs of electrons and no conjugated double bond in extended part (Y), increase the electron density at the ring; and therefore, are strongly activating. Furthermore, these types of groups donate those lone pair of electrons to the π -system, creating a negative charge density at para and ortho sites; and therefore, become ortho/para-directing via resonance. In other words, these groups make these positions more susceptible to an electron-deficient electrophile.

iii) The substituents like $-\text{X}=\text{Y}$, where there is conjugated double bond (w.r.t ring), decrease the electron density at the ring; and therefore, are strongly deactivating. Furthermore, these types of groups accept those electrons from the π -system, creating a positive charge density at para and ortho sites; and therefore, become meta-directing via resonance. In other words, these groups make m-positions more susceptible towards an electron-deficient electrophile.

iv) Alkyl groups as substituents increase the electron density at the ring via hyperconjugation; and therefore, are strongly activating. In other words, these groups make o- and p-positions more susceptible towards an electron-deficient electrophile.

iv) Although the halogens as substituents also have lone pairs of electrons, they decrease the electron density at the ring; and therefore, are strongly deactivating. This is because these types of groups donate those lone pair of electrons to the π -system via resonance (creating a negative charge density at para and ortho sites), but also withdraw electron density via inductive effect which is more dominant. In other words, these groups make these positions (o- and p- to the attached halogen) more susceptible towards the electron-deficient electrophile.

v) The addition of an entering group to a site in an aromatic compound that already has a substituent group (other than H), the attacking group may replace that substituent group but may also itself get expelled or moved to another position in a subsequent step, called '*ipso*-substitution'.

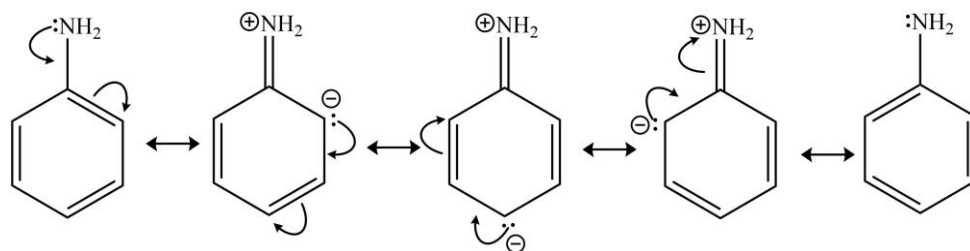
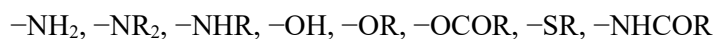


❖ Orientation and Reactivity

The orientation and reactivity in monosubstituted benzene for electrophilic substitution reaction can be divided into four major types as discussed below.

➤ Ring Activator with *o*-, *p*-Directing Influence

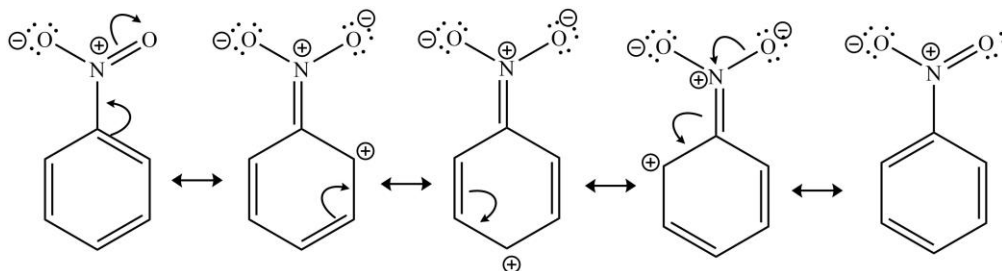
The substituents like $-XY$, where X has lone pairs of electrons and no conjugated double bond in extended part (Y), increase the electron density at the ring; and therefore, are strongly activating. Furthermore, these types of groups donate those lone pair of electrons to the π -system, creating a negative charge density at para and ortho sites; and therefore, become ortho/para-directing via resonance. Nevertheless, one might ask that what if these groups are electron-withdrawing via inductive effect. The answer would be the same (i.e., ring activated) because the electron donation via mesomeric effect is much dominant than the inductive effect in these types of groups. Some typical examples of this type of group are given below with NH_2 as reference.



In other words, we can conclude that these groups make these positions more susceptible to an electron-deficient electrophile.

➤ Ring Deactivator with *m*-Directing Influence

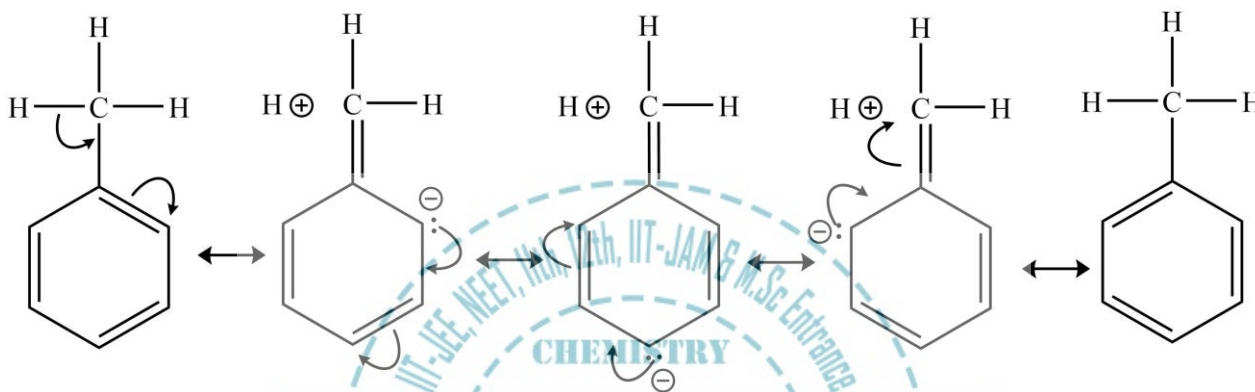
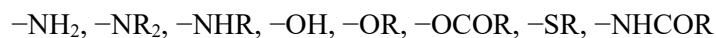
The substituents like $-X=O$, where there is a conjugated double bond (w.r.t ring), decrease the electron density at the ring; and therefore, are strongly deactivating. Furthermore, these types of groups accept those electrons from the π -system, creating a positive charge density at para and ortho sites; and therefore, become meta-directing via resonance. Some typical examples of this type of group are given below.



In other words, we can conclude that these groups make *m*-positions more susceptible towards an electron-deficient electrophile.

➤ **Ring Activator with *o*-, *p*-Directing Influence**

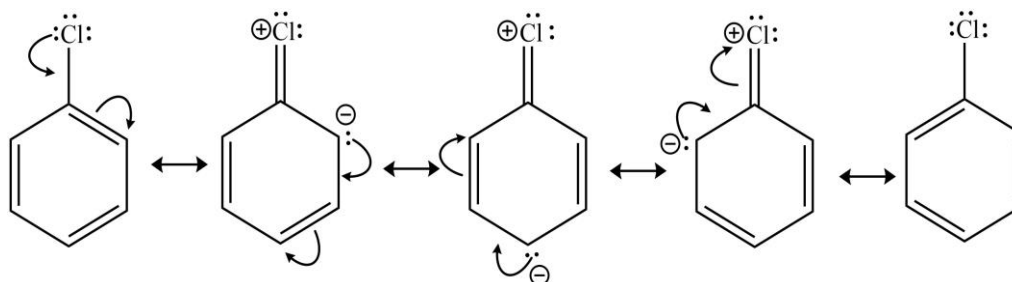
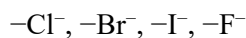
Alkyl groups as substituents increase the electron density at the ring via hyperconjugation; and therefore, are strongly activating. In other words, these groups make *o*- and *p*-positions more susceptible towards an electron-deficient electrophile. Furthermore, these groups are also electron releasing via inductive effect making them highly ring-activating species. Some typical examples of this type of substituents are given below with CH_3 as reference.



In other words, these groups make *o*- and *p*-positions more susceptible towards an electron-deficient electrophile.

➤ **Ring Deactivator with *o*-, *p*-Directing Influence**

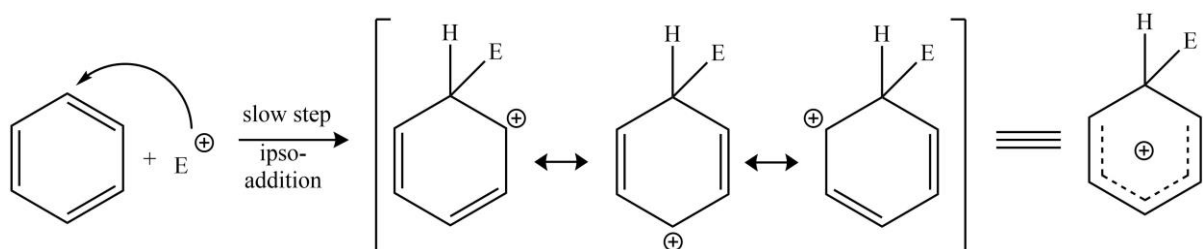
Although the halogens as substituents also have lone pairs of electrons, they decrease the electron density at the ring; and therefore, are strongly deactivating. This is because these types of groups donate those lone pair of electrons to the π -system via resonance (creating a negative charge density at *para* and *ortho* sites), but also withdraw electron density via inductive effect which is more dominant. Some typical examples of these types of groups are given below with CH_3 as the reference.



In other words, these groups make these positions (*o*- and *p*- to the attached halogen) more susceptible towards the electron-deficient electrophile.

❖ Energy Profile Diagrams

The general mechanism for the aromatic electrophilic substitution involves two main steps which must be discussed before we give an energy profile diagram of the same. The electrophile attacks the aromatic ring to form resonance stabilized carbocations, followed by the detachment of leaving group.



A typical energy level profile of various intermediates and transition states in the course of electrophilic substitution reactions in aromatic compounds is shown below.

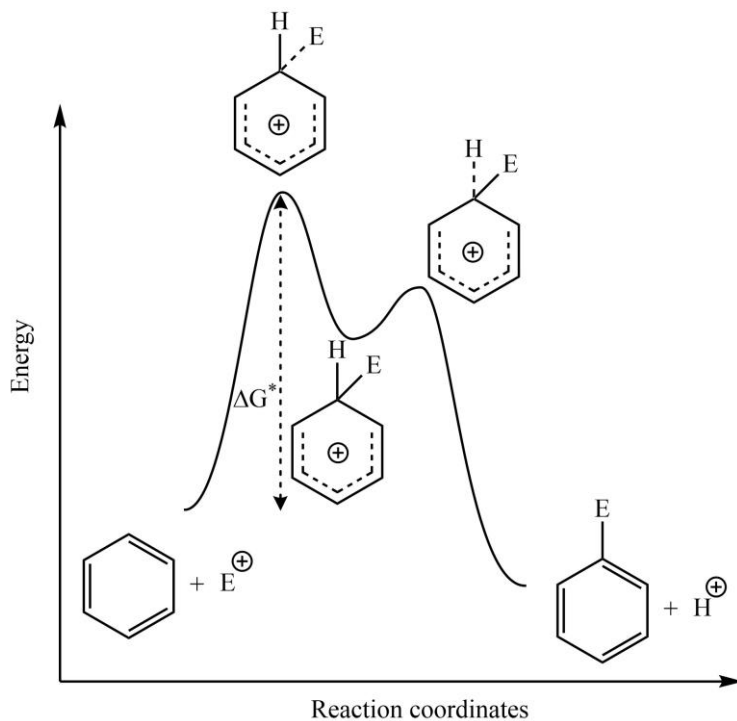


Figure 1. Energy profile diagram for a typical aromatic electrophilic substitution.

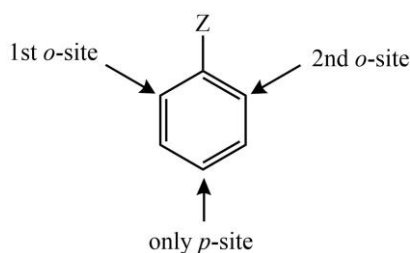
Finally, it is also worthy to note that the rate of electrophilic substitution in already substituted aromatic compounds depends upon the height of the potential barrier which will be different for different types of attack i.e., *o*-, *m*- or *p*-attacks.

❖ The Ortho/Para Ratio

If there is an *o*-, the *p*-directing substituent on the benzene ring, the prediction of the relative amount of both products is quite difficult. This is because the attack at these sites is dictated by many factors like mathematical probability, charge density, steric effects. However, certain conclusions can still be made by considering only one factor at a time keeping others constant. In this section, we will discuss the factors affecting the ratio of *o*- and *p*-products one by one.

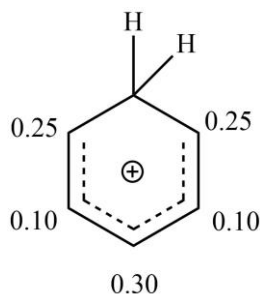
➤ Statistical Factor

One might say the relative ratio of *o*- and *p*-products should be 2:1 because there are two ortho sites but only one *p*- site. However, it is rarely obtained because the actual situation isn't that simple. For instance, consider the chlorination of methylbenzene where statistical treatment will suggest 2:1 *o*-/*p*- ratio but the actual ratio varies from 62:38 to 34:66.



➤ Charge Density

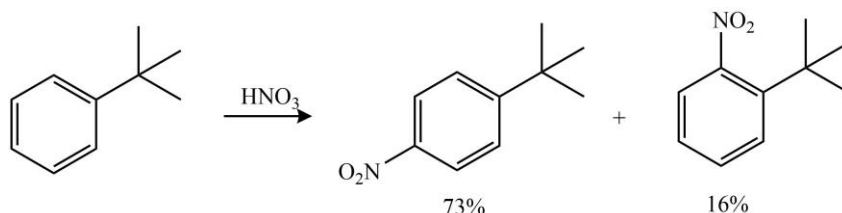
Besides statistical factors, the distribution of charge density at different carbons is of great importance in deciding the attack, which sometimes can completely outrank the former factor. For instance, the charge densities in the phenonium ion are shown below.



It is obvious from the above diagram that a para substituent would show a more significant stabilizing effect on the neighboring carbons than an ortho group. This implies that the *p*-substituted product should be more than 1/3, and the *o*-substituted product should be less than 2/3, provided that other factors like steric hindrance same in both attacks. In hydrogen exchange reactions, the ratio of partial rate factor for *o*-position to the partial rate factor for *p*-position was found to be 0.865 which quite comparable to the ratio of charge densities (i.e., $0.25/0.30 = 0.833$). Similar results were obtained (*o*-/*p*- = 67:33, though the effect was small) if the benzene had *m*-directing groups.

➤ **Steric Factors**

The attack at *p*-position is also supported by the factor steric hindrance which says that bulky will face more crowding at *o*- sites; and therefore, will try to avoid that approach. For instance, the nitration of toluene and tert-butylbenzene results in 58% *o*-product and 16% *o*-product, respectively.



➤ **Loan Pair on *o*-, *p*-Directing Group**

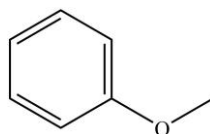
If there is a loan pair on the *o*-, *p*-directing group, the formation of *p*- product is favored at the cost of the ortho. This can be understood by considering the following example.



It is obvious that the A intermediate has an *o*-quinoid structure, whereas B intermediate has a *p*-quinoid structure; since *o*-Quinones are less stable than the *p*-Quinones, B should also be more stable than A, and hence, is expected to contribute more towards the resonance hybrid.

➤ **Substrate's Enclosing**

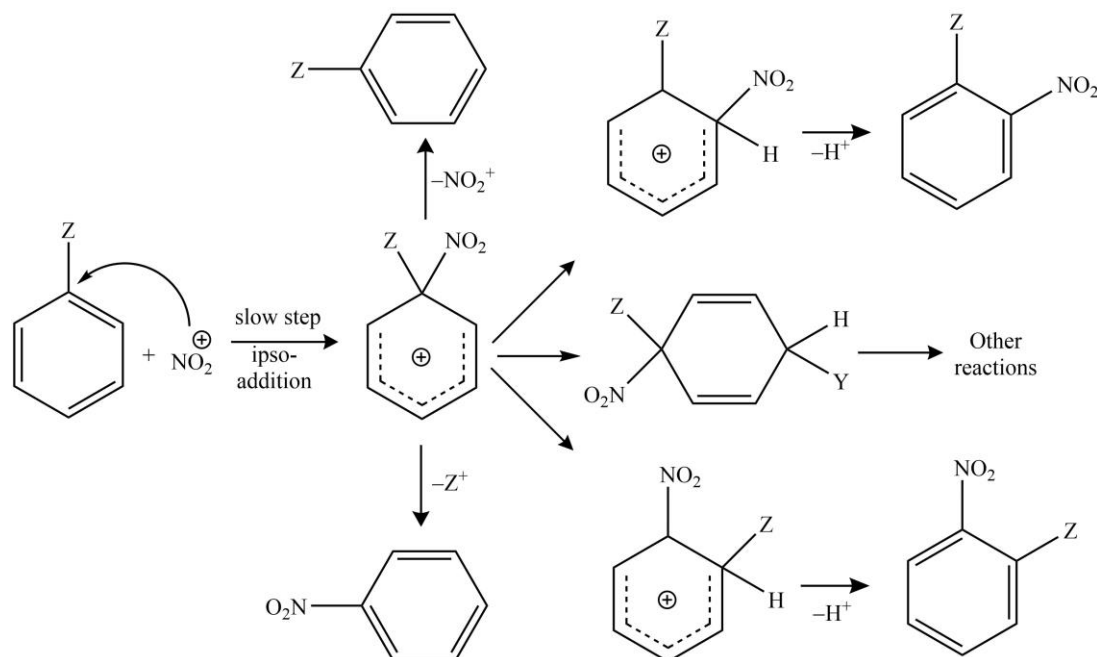
Although it seems impossible but exclusively *p*-products can be obtained enclosing the substrate molecules in a cavity where only the *p*- site is exposed to the electrophile. For instance, the chlorination of Anisole in solutions containing a cyclodextrin *p*/*o*- ratio of 21.656; however, only 1.48 *p*/*o*- ratio was obtained when cyclodextrin was absent.



Anisole

❖ *ipso*-Attack

Besides the attack at *o*-, *m*-, or *p*-positions, the incoming electrophile can also attack the substituted carbon itself called *ipso*-attack. For instance, consider the case when the NO_2^+ group attacks at substituted benzene as given below.



It is obvious that the carbonium ion formed after the attack can result in five different products via five different pathways.

Path I: The NO_2^+ can be lost from arenium resulting in the initial compounds. Since there is no net chemical change, this pathway is quite difficult to detect.

Path II: The NO_2^+ electrophile can show the 1, 2-rearrangement, and losing a proton afterward; and therefore, would result in a product which is equivalent to the product given by *o*-attack. Nevertheless, the amount of *o*-product cannot be predicted exactly though it is quite reasonable. Therefore, an ambiguity arises about the *o*-, *m*-, or *p*-positions because some of the ‘calculated’ *o*-activity may actually be the result of the *ipso*-attack followed by this pathway.

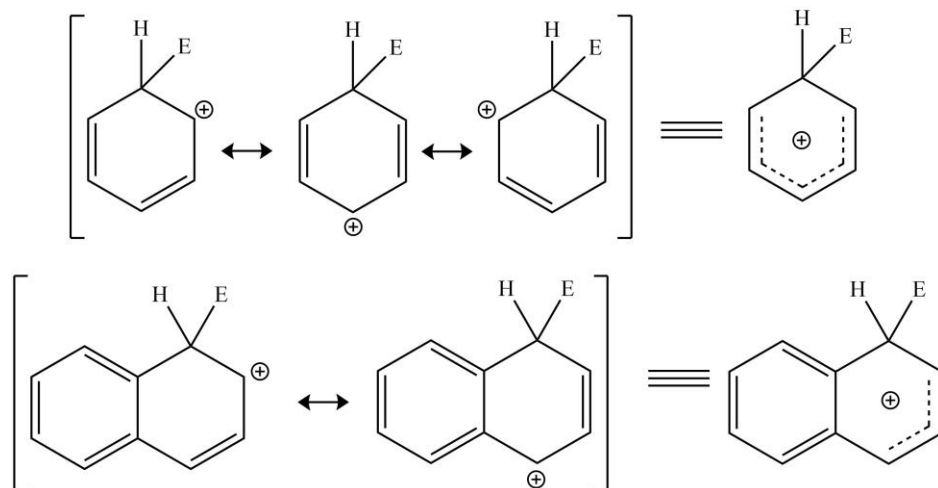
Path III: In this case, Z^+ is lost (instead of NO_2^+) from the arenium ion, resulting in a product that is equivalent to a simple electrophilic substitution where leaving group is not proton.

Path IV: A nucleophilic attack can happen at the carbonium ion, which may result in cyclohexadiene which is equivalent to 1,4-addition to the aromatic ring.

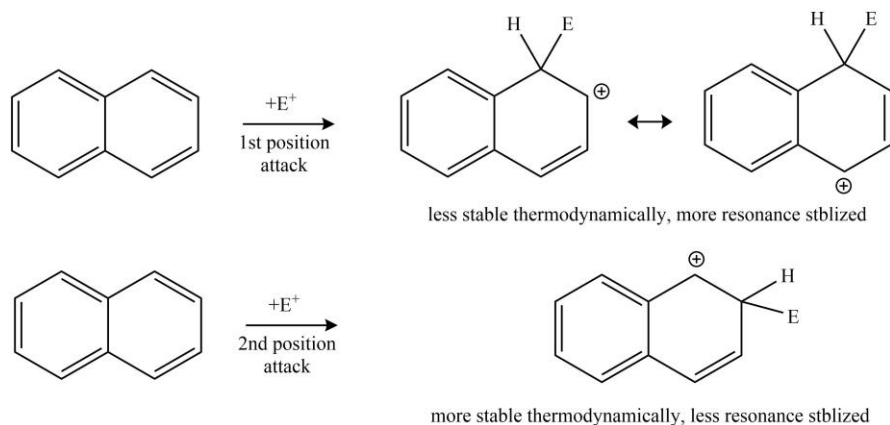
Path V: The Z^+ electrophile can show the 1, 2-rearrangement, and losing a proton afterward; and therefore, would result in a product that is equivalent to the product given by *o*-attack or Path II.

❖ Orientation in Other Ring Systems

The unsubstituted fused ring systems don't have all the sites equivalent like they were in benzene. Therefore, the electrophile will prefer some sites over the others even if single carbon isn't substituted. For instance, the 1st position in naphthalene is more reactive towards electrophilic substitution than the 2nd site. This is because the carbonium ion formed after the attack at 1st carbon has more resonating structures than we would have obtained for the carbonium ion formed by the attack at 2nd carbon.



Nevertheless, the β -position may also become of the highest priority under special experimental conditions. For instance, the sulfonation of naphthalene at 160° gives rise to a β -substituted product; whereas if the same reaction is carried out at 80°C, we get an α -substituted product.



Furthermore, it is also worthy to note that excessive resonance stabilization of arenium ions makes polycyclic conjugated ring systems more reactive toward electrophilic substitution than benzene; and the orientation can be rationalized on the basis of stability of same arenium ions. The same statement is true for heterocyclic ring systems.

❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles

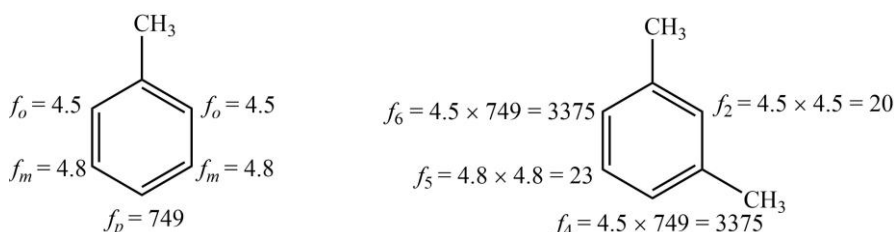
The quantitative treatment of reaction rate in case of electrophilic substitution with reference to substrate structure and attacking electrophile is given below.

➤ *Quantitative Treatments of Reactivity in the Substrate*

Unlike nucleophilic substitution where there is only one leaving group, there are many hydrogens that can leave in electrophilic substitution reactions; and therefore, the quantification of rate-ratios isn't that simple in the later category. For instance, we know the ratio of the total rate of acetylation of toluene to the total rate of acetylation of benzene, but have little to no idea about the rate ratios at individual positions. To do so, we need to carefully analyze the proportion of isomers obtained (for kinetically controlled reactions).

The partial rate factor (for a particular group and a certain reaction) may simply be defined as the rate of substitution at a single site relative to a single site in benzene.

To understand the definition more clearly, consider the case mentioned earlier i.e., acetylation of toluene. The magnitudes of partial rate factors for *o*-, *m*- and *p*-sites are 4.5, 4.8, and 749, respectively; which implies that the overall rate of acetylation of toluene at *p*-site is 749 times faster than what it is at a single site in benzene molecule. However, since there are six positions available in benzene, it will only be 125 (749/6) times faster than the total rate of benzene's acetylation. Furthermore, it is also very important to note that the group is considered as a position-activator if the partial rate factor comes out to be greater than unity, and vice-versa is also true. Hence, we can conclude that the methyl group is definitely a *p*-position activator since the partial rate factor for the same is $749 > 1$. Also, the magnitudes of partial rate factors may vary from reaction to reaction, or in the same reaction at different experimental conditions.



Now, after obtaining the partial rate factors, the ratio of possible isomers (when two or more substituents are attached on the cycle which have presumably independent effects) can be forecasted. For instance, if we consider the case of *m*-xylene, the theoretical values of partial rate factors at each site can be obtained by multiplying those from methylbenzene as shown below. Now we can easily calculate the ratio of different isomeric products arising from the acetylation of *m*-Xylene using the following expression.

$$x_i = f_i / \sum_{i=1}^{i=n} f_i$$

Where x_i and f_i are the mole fraction of isomer arising from the i th type position and 'partial rate factor' for the i th site, respectively.

For instance, the mole fraction of 1-(2,6-dimethylphenyl) ethan-1-one (i.e., 2-isomer) will be obtained by dividing the partial rate factor of the same by the sum of partial rate factors of all positions i.e.

$$x_2 = \frac{20}{20 + 3375 + 23 + 3375} = 0.002944$$

To get the isomeric proportion on the percentage scale, it will be 100 i.e., $0.002944 \times 100 = 0.2944$. Similarly, we can also obtain the percentage of mole fraction for other isomers.

Table 1. Experimental and calculated isomeric mole fractions (%) in the Acetylation of *m*-Xylene.

Site	Experimental	Theoretical
2 nd	0	0.29
4 th and 6 th (same)	97.5	99.36
5 th	2.5	0.34

Finally, the total rate-ratio for the acetylation of *m*-xylene to benzene can also be obtained theoretically sum of all 'partial rate factors' by six i.e.,

$$\text{Rate ratio} = \frac{20 + 3375 + 23 + 3375}{6} = 1132$$

It is pretty much obvious that though the isomeric mole fractions are quite reasonable, the theoretical ratio (1132) is quite different from the actual one 347. This is because the real situation isn't that simple and many other factors like steric hindrance also play an important role.

➤ Quantitative Treatment of Reactivity of the Electrophile

Different electrophiles have different magnitudes of reactivity; for instance, the NO_2^+ ion can react with benzene and also with aromatic rings having deactivating substituents, but the diazonium ions react only with aromatic rings having strongly activating substituents. The Hammett equation can be used to analyze this preferred behavior of attacking electrophiles. To do so, recall the general form of Hammett equation for the cases of *m*- and *p*- $\text{XC}_6\text{H}_4\text{Y}$ (X a variable substituent, and Y is the 'reaction spot' not group) i.e.

$$\log \frac{k}{k_0} = \sigma \rho = \log \frac{K}{K_0} \quad (1)$$

where k and k_0 are the rate constants for the substituent X and X = H; ρ and σ are the constants for reaction conditions and substituent X, respectively. The symbol K and K_0 are the equilibrium constant for the group X and X = H. Furthermore, it should also be noted that since the Hammett equation is for monosubstituted benzene rings, the substrate becomes a simple benzene ring if X = H because 'Y' the reaction spot and not any ring-attached group.

However, the equation given above is for overall rate constants (I mean, for all the available sites); and therefore, if we want to use this equation for single-site comparison, we will need to convert overall rates into partial rate factors first. This can be done by dividing k_0 by 6 (benzene has six equivalents 'reaction spots' i. e. Y), and by dividing k by 2 and 1 for *m*- and *p*- electrophile-attack, respectively (C_6H_5X have two meta and one para site). Now one might ask why we would need to convert overall rate constants into 'partial rate factors, then the answer is the same as we have discussed in the previous section; to find isomeric proportions. Now the isomeric proportions proposed by this equation were quite accurate if X is an electron withdrawing in nature. Nevertheless, large deviations were observed X is electron-donating in nature. In other words, partial rate factors derived from k values given by equation (3) weren't very reliable if group X are electron-donating in nature; and therefore, a modification was needed.



An American chemist, H.C. Brown, solved the problem by introducing modified σ -values labeled as σ^+ , where the plus symbol represents a positive charge appearing in the transition state. Substituents with negative and positive σ^+ -values position activating and deactivating, respectively. In other words, the modified equation can be used to rationalize the aromatic substitution at rings with electron-donating, as well as, electron-withdrawing groups.

Now the question arises, what does the parameter ρ correlates because σ (or σ^+) values are almost exclusively correlated with the reactivity of substrate structure in electrophilic substitution. The answer is, it is connected with the reactivity of attacking electrophile and how it affects the overall reaction-stability. Nevertheless, besides the electrophile, ρ -values may also change with the reaction's experimental conditions. A smaller negative ρ -value implies a less reactive electrophile and vice-versa. Furthermore, it should also be kept in mind that this is true only for meta- and para-sites because the Hammett equation isn't applicable to ortho sites.

Brown developed his idea on the basis of the fact that the reactivity of a particular species shows an inverse variation with selectivity. He observed that all the electrophiles can be classified on the basis of their choice of the attack on benzene vs toluene and ortho- vs para positions (in toluene).

Table 2. Comparative reaction rates and products' ratio in some typical electrophilic substitutions on benzene and toluene.

Reaction-type	<i>m</i> -isomer	<i>p</i> -isomer	$k_{\text{toluene}}/k_{\text{benzene}}$
Bromination	0.3	66.8	605
Chlorination	0.5	39.7	350
Benzoylation	1.5	89.3	110
Nitration	2.8	33.9	23
Mercuration	9.5	69.5	7.9
Isopropylation	25.9	46.2	1.8

It is obvious from the above data that if an electrophile prefers to attack toluene over benzene, it will also prefer to attack *p*-site to give major product, and vice-versa. Brown formulated this observation into the following formula.

$$S_f = \log \frac{f_p}{f_m} \quad (2)$$

Where S_f is the selectivity and $f_{p,m}$ are the partial rate factors. The conclusion from equation (2) is that more reactive species tend to attack meta-position rather than para, and vice-versa is also true. Furthermore, it is also possible to modify the Hammett-brown equation using the above result to prove the following.

$$\log f_p = \left(\frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+} \right) S_f \quad (3)$$

and

$$\log f_m = \left(\frac{\sigma_m^+}{\sigma_p^+ - \sigma_m^+} \right) S_f \quad (4)$$

and

$$S_f = (\sigma_p^+ - \sigma_m^+) \rho \quad (5)$$

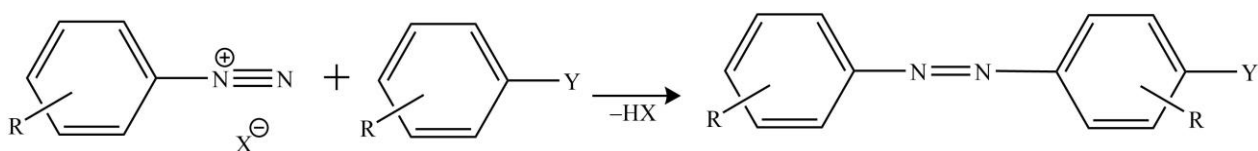
Partial rate factors and ρ -values obtained by employing equation (3–4) were quite comparable with experimental data.

❖ Diazonium Coupling

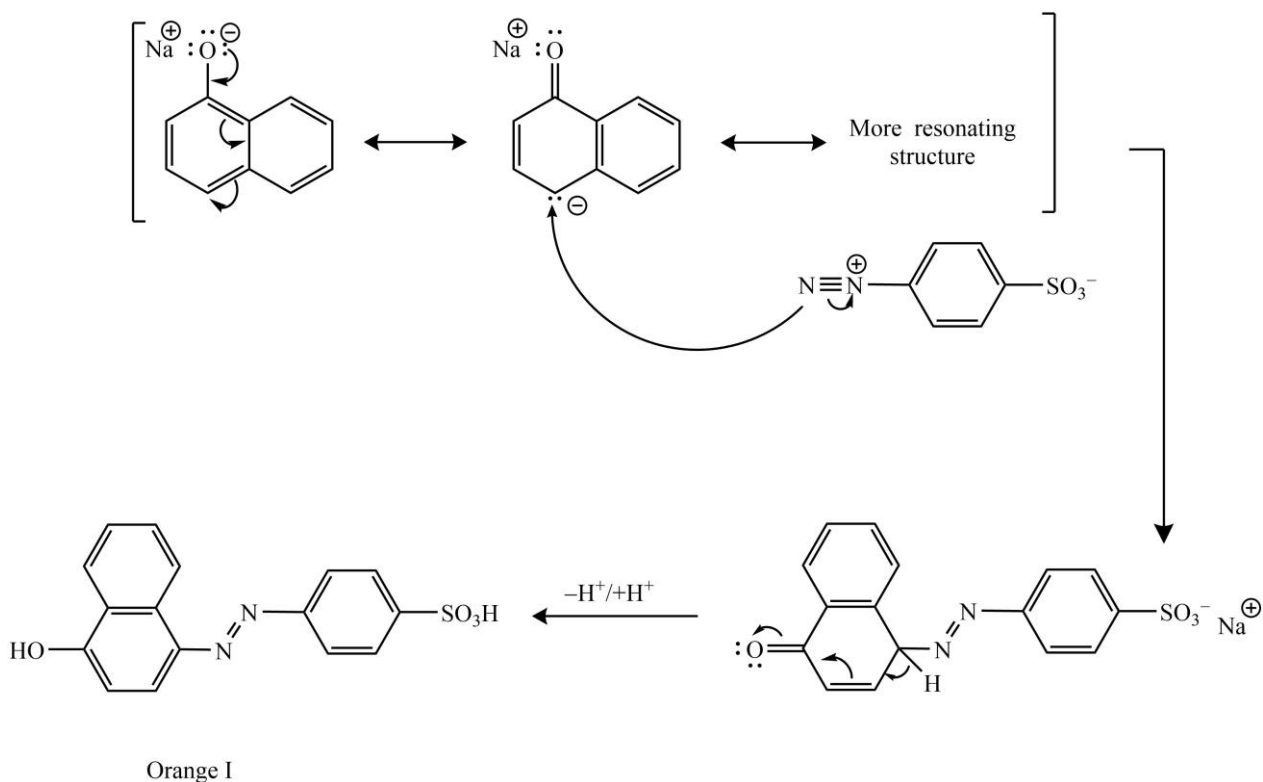
The diazonium coupling may simply be defined as the reaction between a diazonium salt and an aromatic compound to give rise to an azo compound.

In this type of aromatic electrophilic substitution, the aryldiazonium cation acts as the electrophile whereas the activated arene behaves as a nucleophile; and the resulting diazonium compound is also aromatic in most cases.

Illustrative Reaction: The general chemical reaction showing the diazonium coupling in aromatic compounds is shown below.



Mechanism Involved: The mechanism involved in the diazonium coupling reaction that gives rise to Orange I dye is shown below.



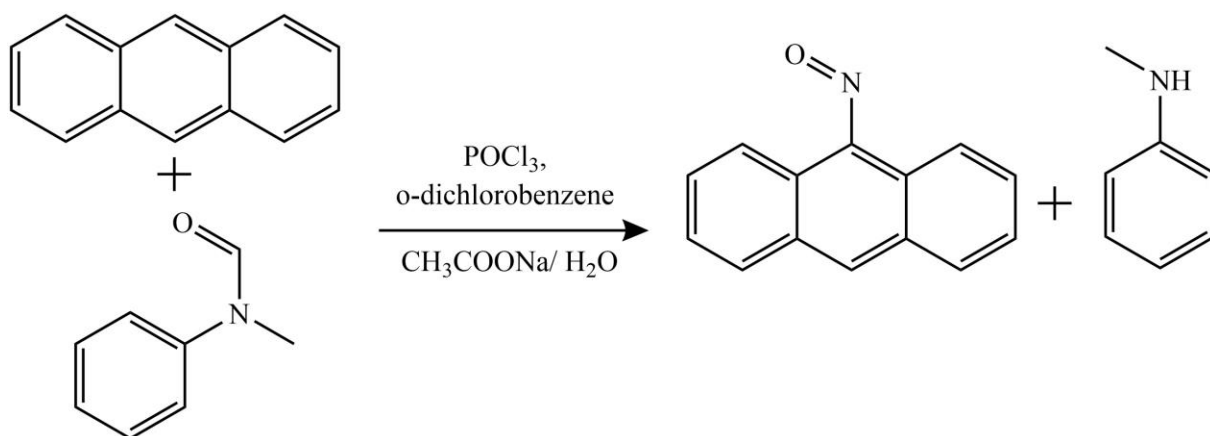
Some of the most important applications of diazonium coupling in industries include the synthesis of dyes, pigments, and lakes.

❖ Vilsmeier Reaction

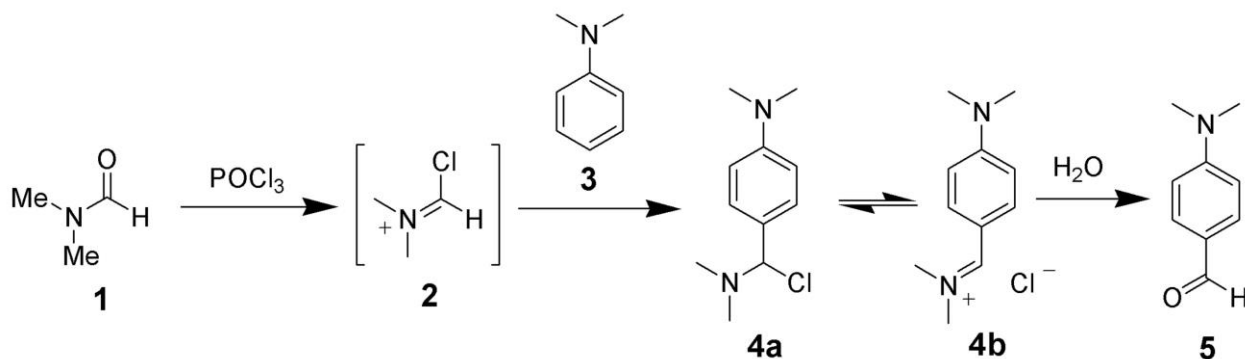
The Vilsmeier (or Vilsmeier-Haack) reaction may simply be defined as the chemical transformation of a substituted amide with phosphorus oxychloride and an electron-rich arene to result in an aryl ketone or aldehyde.

The reaction was invented by Anton Vilsmeier and Albrecht Haack, and therefore, is also named after them. The common examples of the Vilsmeier-Haack reaction include the reaction of benzanilide and dimethylaniline with phosphorus oxychloride to give an unsymmetrical diaryl ketone.

Illustrative Reaction: One of the most popular reactions of this type is the reaction of anthracene with N-methylformanilide, also using phosphorus oxychloride, gives 9-anthracenecarboxaldehyde.



Mechanism Involved: The reaction of a substituted amide with phosphorus oxychloride gives a substituted chloroiminium ion, also called the Vilsmeier reagent.



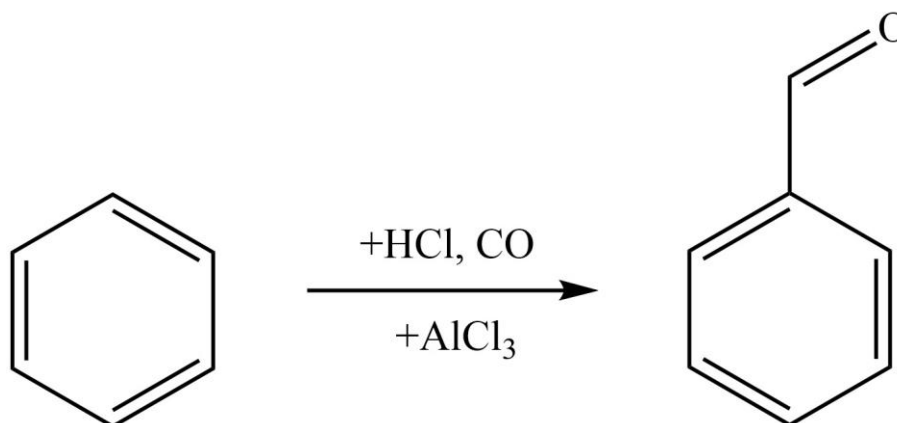
The initial product is an iminium ion, which is hydrolyzed to the corresponding ketone or aldehyde during workup.

❖ Gattermann-Koch Reaction

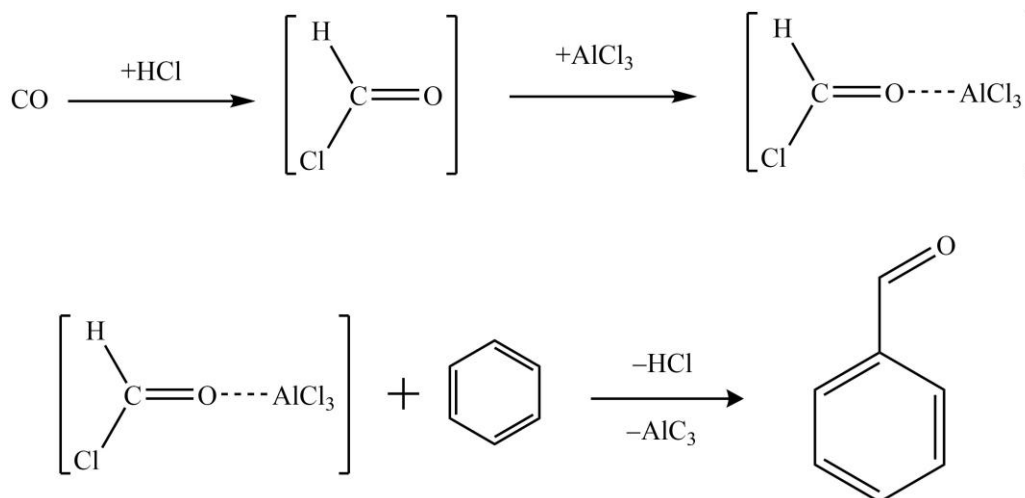
The Gattermann (or Gattermann-Koch) reaction may simply be defined as a chemical transformation in which aromatic compounds are formylated by a mixture of carbon monoxide (CO) and hydrogen chloride (HCl) in the presence of a Lewis acid catalyst such as AlCl_3 .

The reaction was invented by Ludwig Gattermann and Julius Arnold Koch, and therefore, is also named after them. Furthermore, it is also important to note that this reaction is a variant of the Gattermann reaction where HCN is replaced by CO.

Illustrative Reaction: The general chemical reaction showing the Gattermann-Koch reaction in aromatic compounds is shown below.



Mechanism Involved: The mechanism involved in the Gattermann-Koch reaction in aromatic compounds is shown below.



It should also be noted that this reaction cannot be applied to phenol and phenol ether substrates which were common in simple Gattermann reaction. Initially was thought that formyl cation first forms formyl chloride as an intermediate but nowadays it is assumed that the formyl cation directly.



❖ Problems

- Q 1. Define arenium ion. Discuss the organic reaction mechanism involving them.
- Q 2. What are ring activators and deactivators? Explain with suitable examples.
- Q 3. Draw and discuss the typical energy level diagram for the electrophilic substitution.
- Q 4. Define ortho/para ratio. What factors affect this ratio?
- Q 5. State and explain *ipso*-attack.
- Q 6. Discuss the directive influence of substituents in ring systems other than benzene.
- Q 7. Explain the quantitative treatment of reactivity in substrates and electrophiles.
- Q 8. What is diazonium coupling?
- Q 9. Discuss the mechanism of the Vilsmeier reaction.
- Q 10. Write a short note on the Gattermann-Koch reaction.

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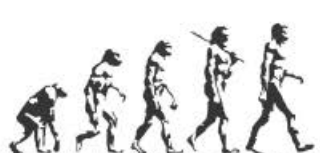
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Volume I

MANDEEP DALAL



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