The Presence of Substituents on the Benzene Ring

Previously we have encountered the electrophilic replacement of hydrogen on a benzene ring. With most electrophiles, this process can be stopped at mono-substitution because the newly introduced group in the benzene ring deactivates the ring, Thereby slowing further reaction. We also saw that alkyls have the opposite effect – positive inductive effect. As a result, in Friedel-Crafts alkylation, higher substitution is difficult to avoid. We say, therefore, that substituent groups affect both **reactivity** and **orientation** in electrophilic aromatic substituents.

What are the factors that contribute to the activating or deactivating nature of substituents on a benzene ring? Furthermore, does subsequent substitution occur at preferred positions around the ring?

What makes a mono-substituent benzene more or less susceptible to further electrophilic attack? What controls the position where an electrophile will attack next?

The rate at which a second substituent can be introduced into a C_6H_6 ring and the position of the second substituent, relative to the first, is determined by the substituent already present in the ring.

It is the *substituent* on the ring, which has either an activating effect, by donating electron density, or a deactivating effect, by withdrawing it, and which directs incoming electrophiles to specific positions.

Hence, a substituent already present on the benzene ring can have two possible effects:

1. The substituent present can alter the reactivity of the C_6H_6 ring – make it more or less reactive i.e. to say it can activate or deactivate the ring.

2. The other effect is the position where reaction occurs with the second substituent. With the first substituent present, there are three possible position of attack ...

1,2 – position	1,3 – position	1,4 – position
ortho-	meta-	para-

The three products are not formed at random, rather a given substituent already present on the benzene ring usually directs the position of the second substituent.

All reactions with C_6H_6 are electrophilic as established, therefore what effect would you expect to make the reaction faster?

-Whether the C_6H_6 ring becomes more or less negative than before, if it becomes more electron rich i.e. a group present which releases electrons towards the C_6H_6 ring, therefore attack by electrophile is quickened; and those that deactivate the benzene ring are electron withdrawing groups i.e. the ring is electron poor, thus less reactive towards electrophiles.

An electron-releasing group is one that has a negative charge or δ- a charge direction attached to a C_6H_6 ring, i.e. pushing electrons onto the ring, thus activates the ring towards electrophilic substitution (relative to benzene itself).

An electron withdrawing group is one that has a positive or δ+ charge directly attached to the benzene ring i.e. negative charge is withdrawn from the π-orbitals of the benzene ring, which will be left with a small positive charge making the benzene ring less susceptible to attack by an electrophile, thus deactivating the C_6H_6 ring.

The substituents which increase the reactivity, direct further substituents predominately into the ortho- and para- positions i.e. the 2,4,6 – positions, whereas those substituents which deactivate the ring always produce meta- products i.e. into the 3 or 5 – positions.

Common substituents in order of electron donating or withdrawing power

Electron Donating Decreasing Power Electron withdrawing ↓	-OH -NH_2 -OCH_3 -CH_3 -Cl -CHO -SO_3H -NO_2 -COOH	↓ ↓ ↓ ↓	Decreasing Rate of

Directive effects of some common substituents

Meta- directing	**Ortho -Para-directing**
-NO_2	- CH_3
-COOH	- OCH_3
-CHO	- Cl
-CN	- NH_2
-SO_3H	-OH

How substituents increase the reactivity of the benzene ring?

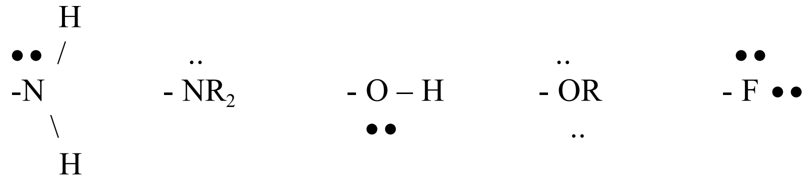
We can account for the electron-withdrawing and electron-releasing properties of groups on the basis of two factors: inductive effects and resonance effects.

1. if the attached group is electron donating, example, a methyl, CH_{3-} group is a strong electron – electron donating group (note: the electrons lie closer to the C_6H_6 nucleus than on the CH_{3-} group). As the chain gets longer the electron- donating effect weakens.

2. if the substituent attached to the ring has some lone pair electrons which could be lent down, example - NH_2, - OH, -OCH_3, -NR_2, -NCO (an amide). The lone pair of electrons on these groups may participate in resonance with the ring. Thus, the -OCH_3 group activates the ring to a greater extent than the –CH_3 group, because - OCH_3 has unshared electrons which can be 'lent' to the ring. All of these ortho-para directors have at least one pair of nonbonding electrons on the atom attached to the benzene ring.

Here there are two factors acting in opposition to each other:

1. lone pair of electrons being "lent" to the ring,
2. if the substituent is electronegative, then it's electron – withdrawing effect is always less than the effect of sharing lone pair of electrons.



most electron donating ---------------------------> least electron donating

These three atoms can lend a lone pair of electrons so their lending effect will be the same, however consider the electron withdrawing effect of the three atoms: F > O > N, this is going to act in opposite direction. Hence the atom which is going to activate the ring most is the nitrogen atom followed by the oxygen and then by fluorine.

Substituents which deactivate the benzene ring are strongly electronegative, also none of these groups have lone pairs on the atoms attached to the C_6H_6 ring.

Example: -COOH -NO_2 -CN -SO_3H

None of these atoms attached to the C_6H_6 ring has lone pair of electrons (it does not matter if the atoms attached to other atoms than the one directly attached to the C- atom of the ring has lone pair of electrons.

There is always an exception: Halogen substituents, although deactivating, direct ortho and para.

Halogen substituents inductively withdraw electron density, however, they are donors by resonance. On balance the inductive effect wins out, rendering haloarenes *deactivated*. Nevertheless, the electrophilic substitution that does take place occurs mainly at the ortho- and para- positions

Summary of Effects on Orientation and Reactivity

The presence of a substituent in the benzene ring affects…

1. the *rate* of electrophilic substitution reactions,
2. the *position* of entry of further substituents in the ring.

Full or partial (+) charge on directly attached atom	At least one nonbonding pair on directly attached atom	Alkyl or Aryl
	Halogen , $-NH_2$, - OH, etc.	

<----meta directing -----> <---- -- ortho-para directing ------------------>
<---------- deactivating ------------------> <--------- activating ---------->

Assignment

1. Benzene can be nitrated quite readily to give nitrobenzene but the introduction of a second nitro group, $-NO_2$, into the ring is much more difficult than the first due to the deactivating effect of the $-NO_2$ group already present in the ring. Further substitution will thus produce:

2. The introduction of an alkyl group into the benzene ring has an activating effect on the ring and toluene can be nitrated more readily than benzene giving ultimately…

3. The electron releasing –OH group has an activating effect on the benzene ring making further substitution easier, so that phenol, can be readily chlorinated to give a white precipitate of 2,4,6-trichlorophenol (TCP).
   Phenol reacts readily with concentrated nitric acid, HNO_3, producing 2,4,6-trrinitrophenol, also known as picric acid. This yellow crystalline material detonates powerfully when shocked or heated and has a long history of use as both a military and industrial explosive. The use of picric acid in artillery shells during World War I created an unprecedented demand from the chemical manufacturing industry for phenol.

4. The carboxyl group, -COOH, in benzoic acid, C_6H_6COOH, deactivates the ring, thus the nitration of benzoic acid takes place at about 1/100th the rate of benzene and give predominantly…

5. Bromination of aniline would result in the formation of…

6. Chlorobenzene with conc. $HNO_{3(aq)}$ would predominately produce…

7. What is the predicted rate of bromination for chlorobenzene, phenol and benzene. Classify in increasing order of reactivity. Explain your answer.