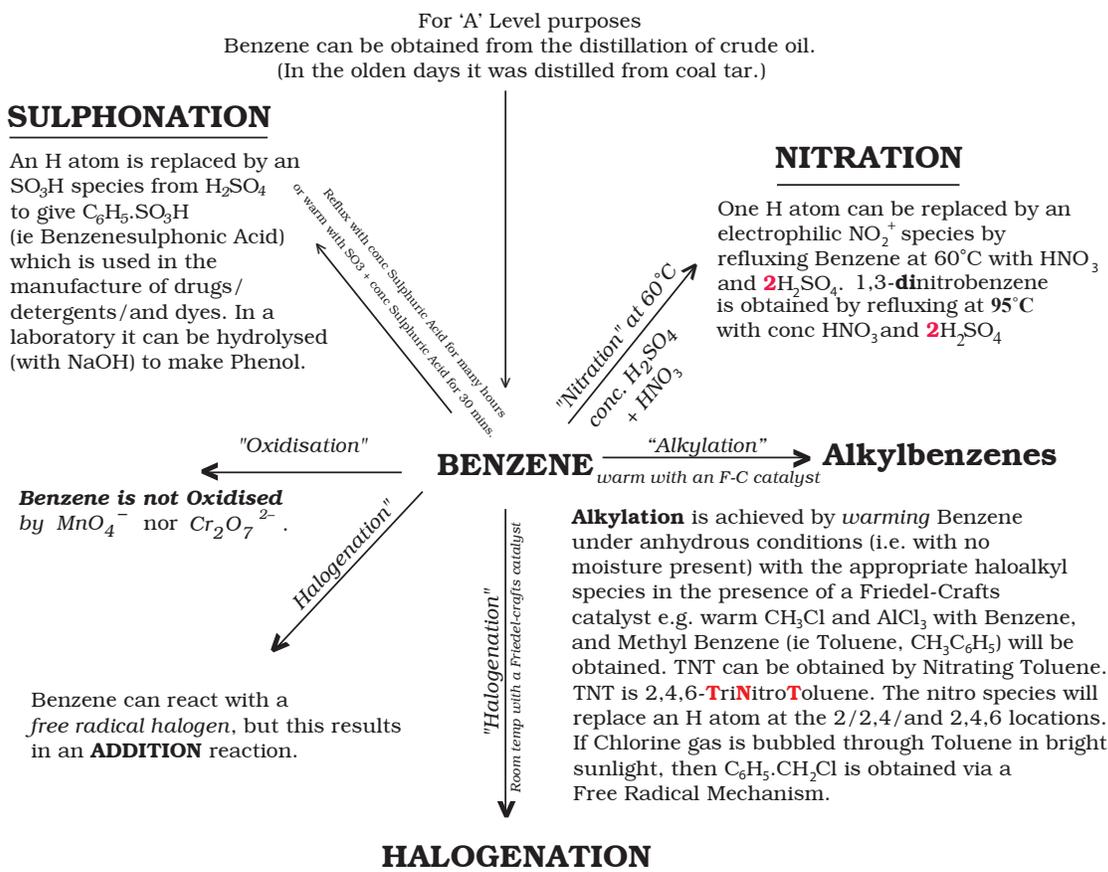


[A Second Year blog on Benzene, C₆H₆, Part 3: 29th December 2018](#)

(This is a revision blog. It is merely a summary of some of the things that you need to know about Benzene.)

This blog is about the “activation” and “deactivation” of the Benzene ring, and then when you understand that, you will find it much easier to go on to understand how you go from Benzene to Phenol and onto Azo dyes (the subject of Blog No 4 on Benzene). However, let me start by reminding you of two Benzene info trees.

The SUBSTITUTION reactions of Benzene



HALOGENATION

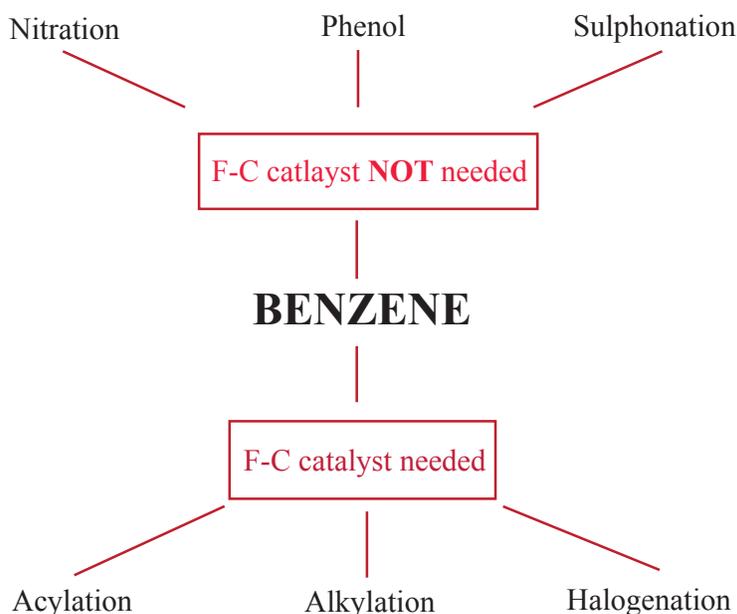
Benzene is much more stable than an Alkene therefore it does not react with a Halogen by itself, but it will react with a Halogen that is attached to a Friedel-Crafts catalyst (i.e. a Halogen carrier).
Br₂ and FeBr₃ will react with Benzene to replace an H in C₆H₆ with a Br. (C₆H₅.Br is produced.)
Cl₂ and AlCl₃ will react with Benzene to replace an H in C₆H₆ with a Cl. (C₆H₅.Cl is produced.)
The Halogen molecule forms a dative bond with the Friedel-Crafts catalyst and this creates a separation of charge in the Halogen molecule, and it is the “+” part of the Halogen molecule (ie the *electrophilic* part of the polarised molecule) that now attacks the Benzene ring.

ADDITION REACTIONS

- Benzene will react with **Hydrogen** gas at 150°C in the presence of finely powdered Nickel to give C₆H₁₂.
- Benzene will react with a **Halogen** gas via a Free Radical Mechanism to give for example 1,2,3,4,5,6-hexachlorocyclohexane (with an H and a Halogen at each of the six apices).

NB Benzene is not oxidised by Potassium Permanganate nor by Potassium Dichromate, but the -CH₃ group in *Toluene* will be oxidised by an alkaline manganate ion to give Benzoic Acid (C₆H₅.COOH).

EAS Reactions of Benzene



What is “activation” and “deactivation”?

If for some reason a species becomes attached to a Benzene ring (via an EAS reaction), and it then/ thereby increases the electron density of the delocalised π ring on Benzene, then the Benzene π ring is said to become “**activated**”. On the other hand, if the species reduces the electron density in Benzene’s π ring, then the Benzene ring is said to be “**deactivated**”.

The **activation** (the increase in electron density of the π ring) and the **deactivation** (the reduction in electron density of the π ring) is entirely dependent on the substituent species. If the species that has replaced one of the H atoms on the Benzene ring is able to push electron density into the π ring or withdraw electron density from the π ring, then that is when activation and deactivation will occur.

Please read Chapters 3 and 8 of the Second Year book on Organic Chemistry for the full details, but in essence

where there is a **positive** Mesomeric effect, then the Benzene π ring becomes **activated** at positions 2/4/6 and

where there is a **negative** Mesomeric effect, then the Benzene π ring becomes **deactivated**, but it will become **activated** at positions 3 and 5.

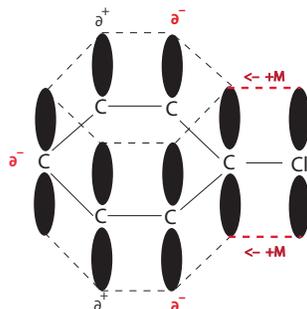
NB Please be very careful about the terminology used in this topic. For some reason, American chemists refer to the phenomenon of activation and deactivation as “electron donating” and “electron withdrawing”. However, please make sure that you understand that **no electrons are donated and no electrons are withdrawn**. If they were, then ions would be formed – and here no ions are formed.

All that happens is that **electron DENSITY is increased** and **electron DENSITY is reduced**.

A positive M (+M) effect

A **positive M** effect on Benzene's π ring will happen if an unhybridised 'p' orbital in the substituent species overlaps the unhybridised 'p' orbital of the C atom in Benzene to which it is attached, because the electron in the substituent's unhybridised 'p' orbital (in effect) *swims over* into Benzene's π ring (as though it owns it) and increases the electron density. This can be seen most clearly by looking at a halogenated Benzene ring i.e. $C_6H_5.Cl$ or $C_6H_5.Br$ or $C_6H_5.I$.

C_6H_5Cl has been activated at positions 2/4/6 on the Benzene ring



It is the overlap in the Cl atom's unhybridised 'p' orbital with the 'p' orbital in the C atom to which it is attached that causes the +M effect. C_6H_6 is now activated at positions 2/4/and 6. (2/4/6 become ' δ^- '.)

The species that cause activation are species such as

- **Alkyl Groups** (i.e. $-C_nH_{2n+1}$)
- **A Halogen species** (i.e. $-Hal$)
- **Any species that contains an electron in a 'p' orbital that lies in the same vertical plane as the 'p' orbitals in the Benzene π ring** (e.g. $-O-$, $-OH$, $-NH_2$, $-O-C_nH_{2n+1}$, $-OR$, $-NHR$, $-NRR$, etc.¹) because their lone pairs get locked into the benzene π ring and increase its electron density (and this is a +M effect). **However, for activation to occur, the atom attached to the substituent atom must not be more electronegative than the substituent atom. If it is more electronegative, then deactivation will occur.**

Let us now look at the negative M ($-M$) effect, but here is a little hint to make it very easy to spot when there is going to be a $-M$ effect.

Look not at the atom that is attached to the C atom in the Benzene ring (i.e. do not look at the substituent atom). **Instead, look at the atom next to it! If that atom is more electronegative than the substituent atom then deactivation will occur. If it is not more electronegative than the substituent atom then activation will occur.**

- OK, now to test whether or not you have understood what I have just told you, please work out
- if " $-NO_2$ " is the substituent species will it activate or deactivate the Benzene ring?
- and
- if " $-NH_2$ " is the substituent species will it activate or deactivate the Benzene ring?
- and what is *your* explanation for your answer?**

This is a very simple test that I set my students every year. It unfailingly shows whether or not they have understood when activation and deactivation occur.

OK, now read on!

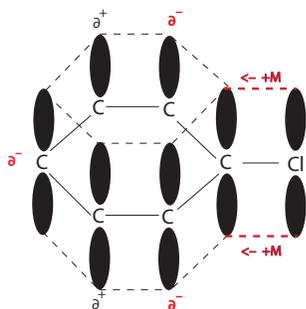
¹ where "R" here is any alkyl group.

A negative M (-M) effect

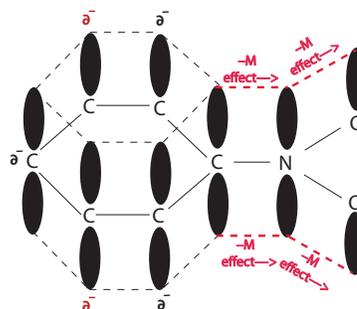
A **negative M** effect on Benzene's π ring will happen if an unhybridised 'p' orbital in the substituent species overlaps the unhybridised 'p' orbital of the C atom in Benzene to which it is attached, and the atom attached to the substituent atom is more electronegative than the substituent atom because the more electronegative atom pulls electron density off the substituent atom and this in turn pulls electron density off Benzene's π ring.

Let us see how it works in the examples that I set you just now.

C₆H₅Cl has been activated at positions 2/4/6 on the Benzene ring



Deactivated C₆H₅.NO₂ is activated at positions 3 and 5



C₆H₅.NH₂ (Phenylamine/Aniline)	C₆H₅.NO₂ (Nitrobenzene)
The unhybridised 'p' orbital in the substituent atom overlaps the unhybridised 'p' orbital of the C atom to which it is attached and (because the H atoms are not more electronegative than the N atom) the electron in N's 'p' orbital swims around in Benzene's π ring and increases the electron density of the π ring .	The unhybridised 'p' orbital in the substituent atom overlaps the unhybridised 'p' orbital of the C atom to which it is attached, but (because the O atoms are more electronegative than the N atom) the electron in N's 'p' orbital is pulled towards the O atoms and this in turn pulls electron density off the Benzene π ring, and thus the electron density of Benzene's π ring is decreased .
Activation occurs at 2/4/and 6.	Activation occurs at 3/and 5.

That is all that there is to activation and deactivation!

There are roughly 7.5 billion human beings on the face of this planet, and because **you** have taken the trouble to master this topic, my guess is that you now know more about activation and deactivation than probably 7,499,750,000 other human beings on earth. *Isn't that exciting!*

In one of the Chapters of my Second Year book I say

“When I was young I was considered to be quite intelligent, but when I got to University I found that there were people who were **MILES** ahead of me. The same was true when I left University and went to work. The thing that I am trying to do with you is to make sure that when you get to University and to work, it is **YOU** who are streets ahead of the others.”

Inevitably there will always be people who are more intelligent than you are. There is nothing that you can do about that. What I found during my life was that even though other people may be more intelligent than you are, you can be more successful they they are by working harder than they do. Intelligence and hard work combined will always beat intelligence by itself. If you think that Stephen Hawking got to where he did without working extremely hard, then you have as yet not grasped the essence of “success”.

The table below is from UC Davis (but you will have to remember that “ortho-para” means “Activates at 2/4/6”, and “meta” means “Activates at 3/5”. If you have understood what you have read in this blog, then you will straight away understand what it says. I do not like the old Greek references to “ortho” / “meta” /and “para”. I prefer to use a numbering system to indicate positions on a Benzene ring. Please remember that position No. 2 to a person looking at the front of a Benzene ring is position No. 4 for a person looking at the Benzene ring from the back of it, and since there is no “front” and “back” in space, then Position No. 2 is equivalent to Position No. 4, and Position No. 3 is equivalent to Position No. 5.

Table of Substituents

Ortho-Para Directing				Meta Directing	
Strong Activating	Moderately Activating	Weakly Activating	Weakly Deactivating	Moderately Deactivating	Strongly Deactivating
-NH ₂ -NHR -OH -OCH ₃	-NHCOR -OCOR	-CH ₃ -phenyl	-F -Cl -Br -I	-COH -COCH ₃ -COOCH ₃ -SO ₃ H	-NO ₂ -CF ₃ -CCl ₃

However, as with all the rules in Chemistry, there are a lot of factors that are involved, and this is a rough guide as to how often you get what. You are **not** required to know this table for the UK ‘A’ Level exams.

Y in C ₆ H ₅ -Y	Reaction	% Ortho-Product	% Meta-Product	% Para-Product
-O-CH ₃	Nitration	30-40	0-2	60-70
-O-CH ₃	F-C Acylation	5-10	0-5	90-95
-NO ₂	Nitration	5-8	90-95	0-5
-CH ₃	Nitration	55-65	1-5	35-45
-CH ₃	Sulfonation	30-35	5-10	60-65
-CH ₃	F-C Acylation	10-15	2-8	85-90
-Br	Nitration	35-45	0-4	55-65
-Br	Chlorination	40-45	5-10	50-60

The way to read the table is as follows: look at the 3rd and 4th entries in the table and say to yourself

If you were to Nitrate C₆H₅.NO₂ then because it is **deactivated** the Nitration will occur mainly at 3 and 5, but

If you were to Nitrate C₆H₅.CH₃ then because it is **activated** the Nitration will occur mainly at 2/4/and 6.