Unlocking Aromatic Alchemy: The Art of Electrophilic Substitution

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(M.Sc. Chemistry IInd Sem)

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Why do aromatic compounds undergo electrophilic substitution?

- Because of their delocalized pi electron system, which makes them electron-rich and therefore very attractive to electron-deficient species (electrophiles), aromatic compounds undergo electrophilic substitution.
- Rather than breaking their stable aromatic structure through addition reactions, they prefer to react with electrophiles by substituting a hydrogen atom on the ring.

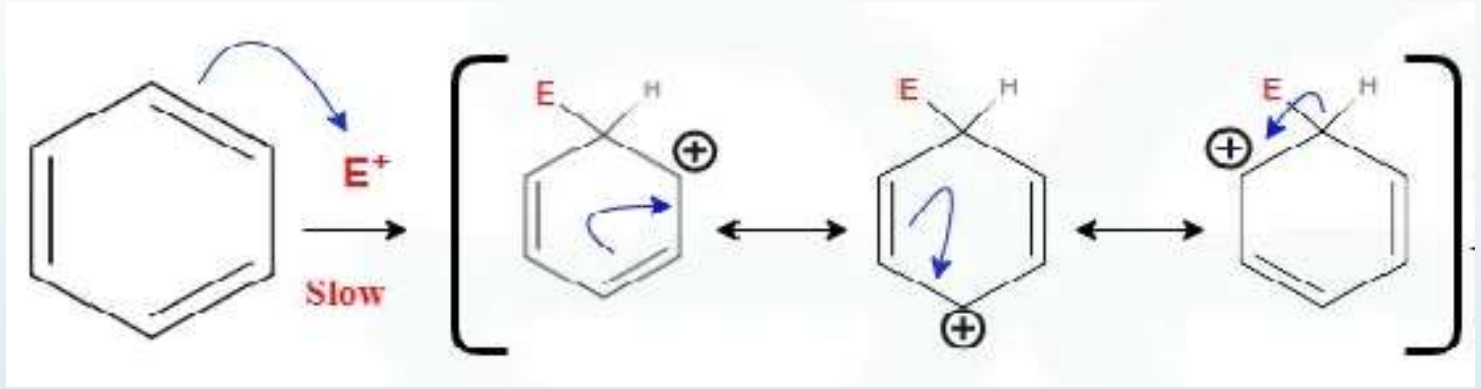
Aromatic Electrophilic Substitution (AES) Reaction

Electrophilic substitution is a fundamental reaction in organic chemistry where an **electrophile** replaces a hydrogen atom in an **aromatic ring**. This process is crucial for synthesizing a variety of compounds, making it a cornerstone of aromatic chemistry.

Basic reaction in Aromatic Electrophilic Substitution (AES)

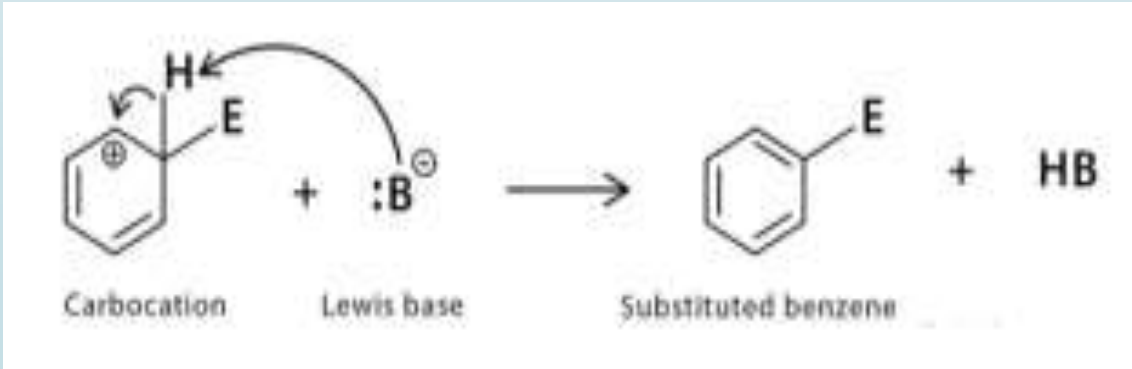
ARENIUM ION MECHANISM OF AES REACTIONS

STEP I: Attack of electrophile onto the pi electrons of the benzene ring to form an intermediate resonance stabilized carbocation intermediate (σ-complex)

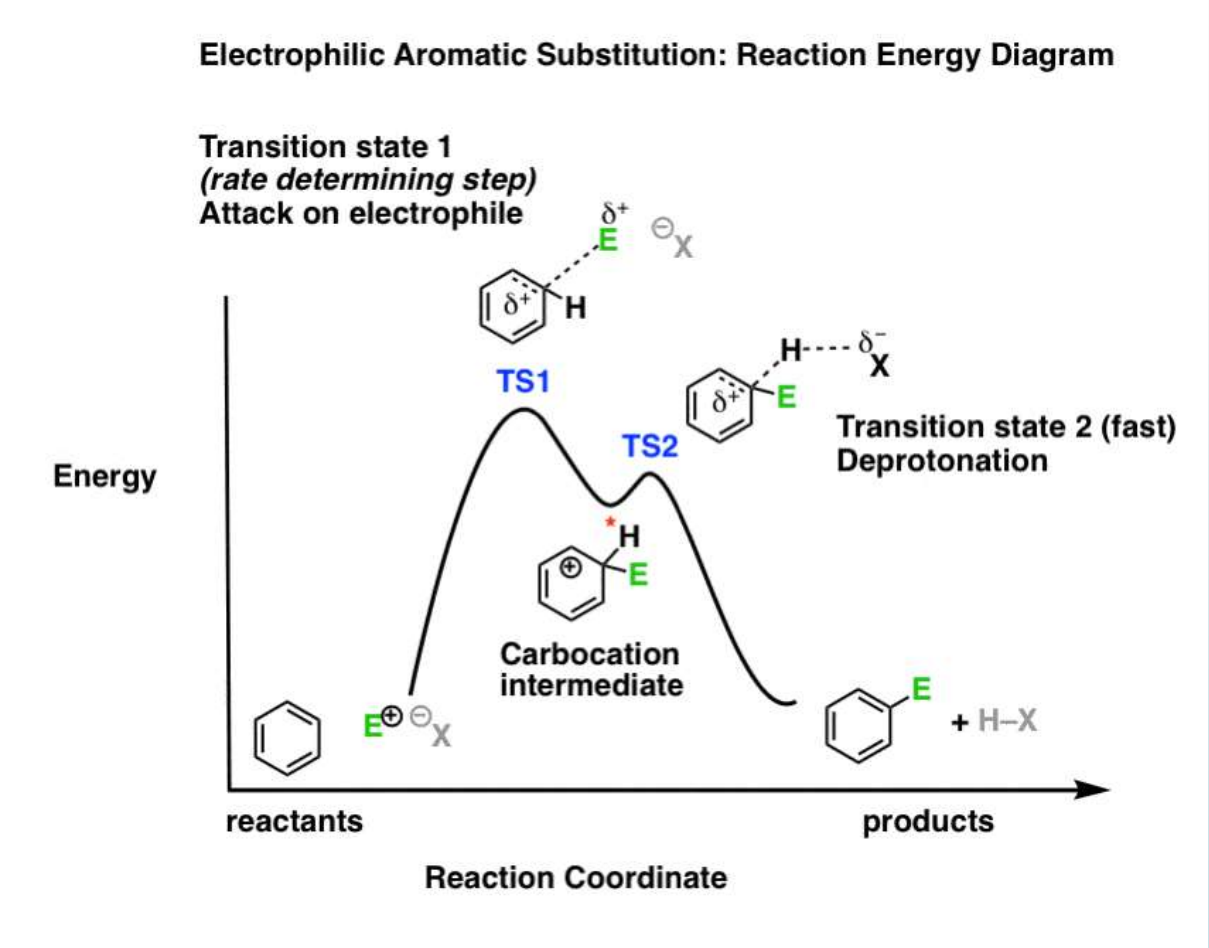


Carbocation (σ-complex)

STEP II: Rearrangement and departure of leaving group (electrofuge)



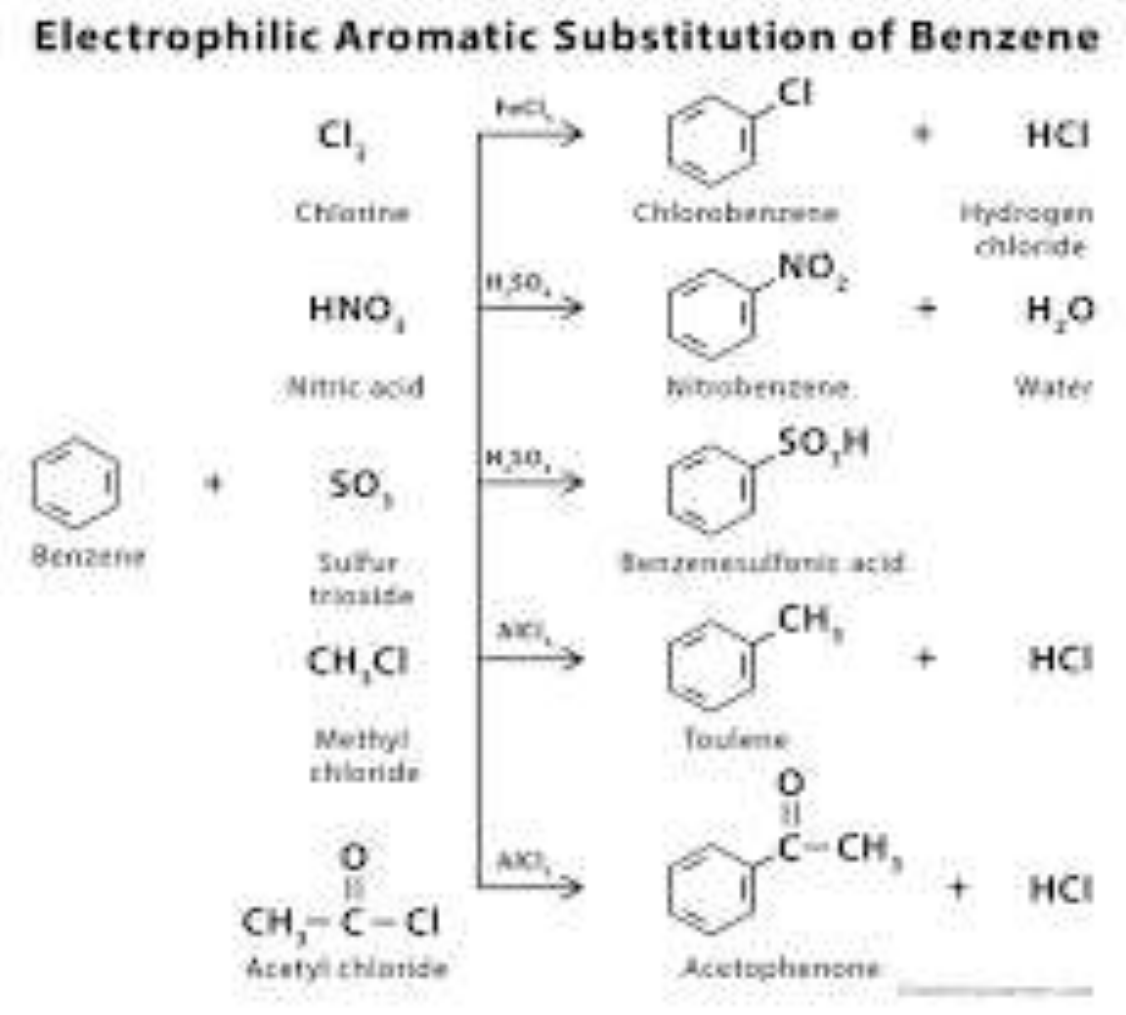
ENERGY PROFILE DIAGRAM



Key Electrophiles in Reactions

Common **electrophiles** include **halogens**, **sulfonic acids**, and **nitronium ions**. Each electrophile has distinct properties that influence the outcome of the substitution reaction. Knowing these can help in designing effective synthetic pathways.

Common Aromatic Electrophilic Substitution (AES) Reactions



Chlorination

Nitration

Sulfonation

Friedel-Crafts Alkylation

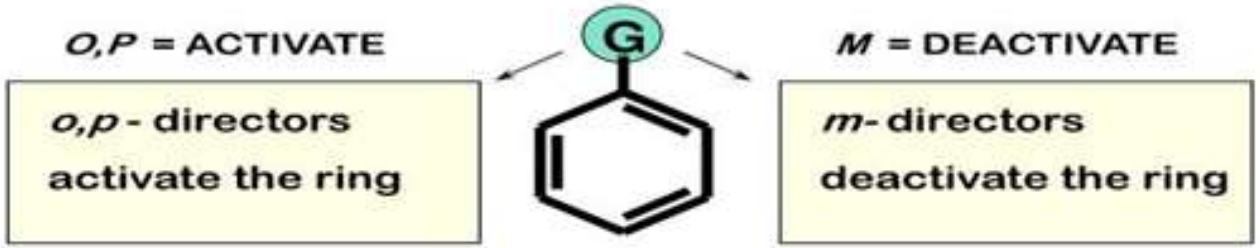
Friedel Crafts Acylation

Factors Influencing Reactions

Several factors affect electrophilic substitution, including **substituent effects**, **reaction conditions**, and **steric hindrance**. Understanding these influences helps chemists predict and control reaction outcomes effectively.

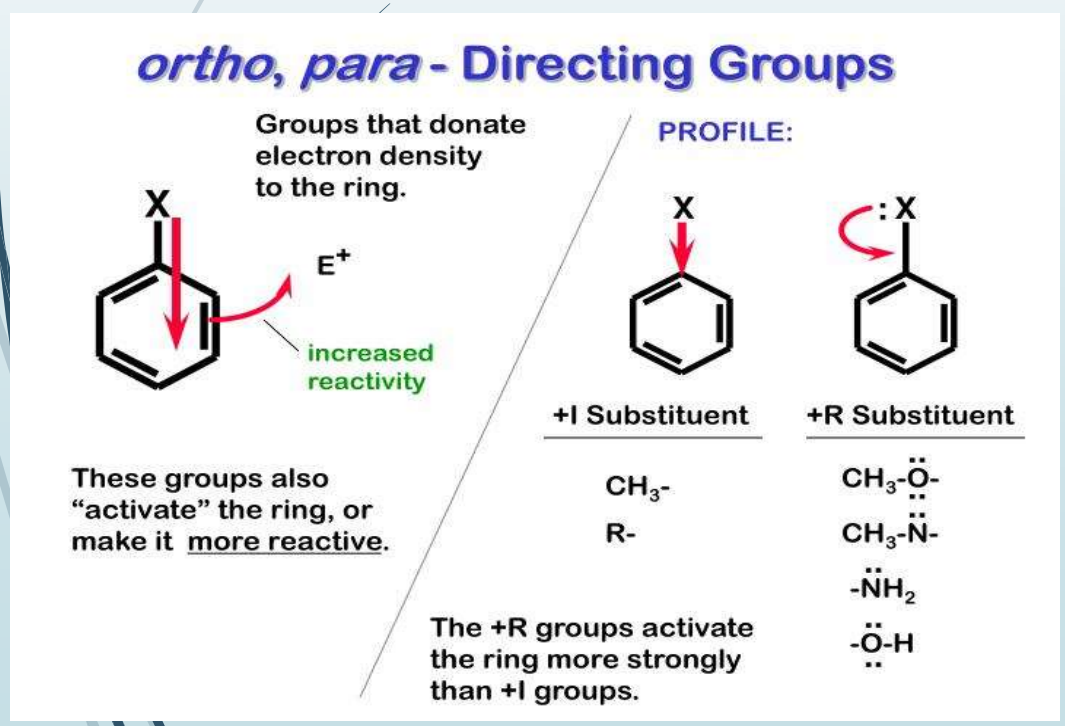
SUBSTITUENT CATEGORIES

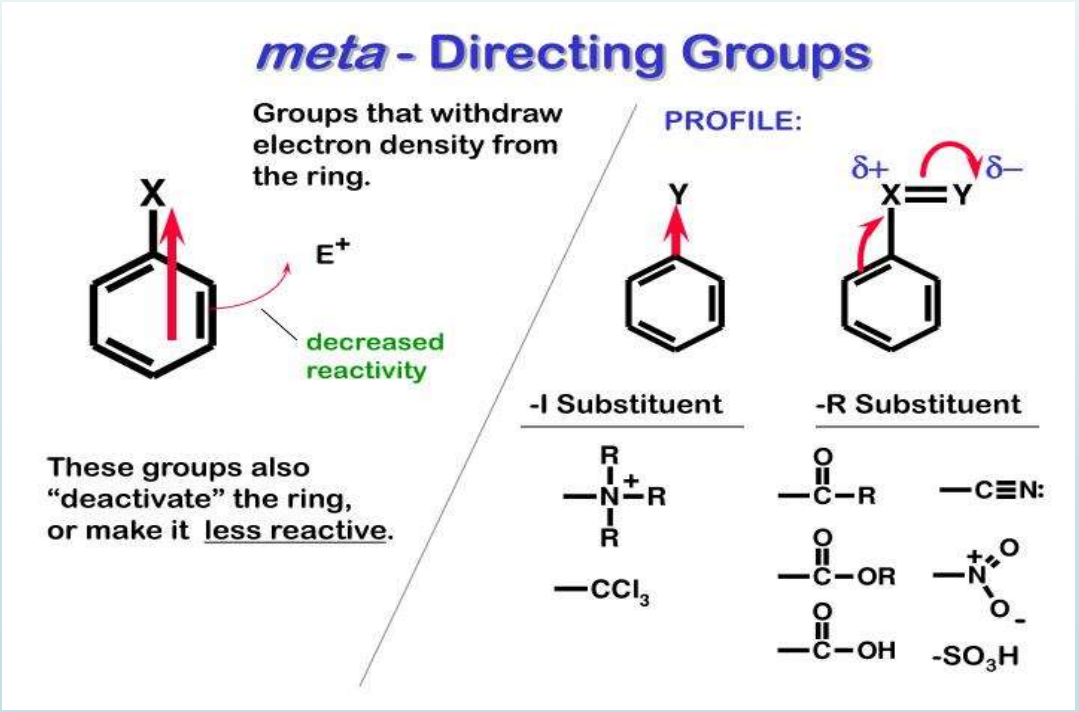
Most ring substituents fall into one of these two categories:



ACTIVATING AND DEACTIVATING GROUPS IN AES REACTIONS

- In essence, the reactivity of the aromatic ring is greatly influenced by electron-donating (**ACTIVATING GROUPS**) groups attached to it, which can direct the incoming electrophile to specific positions (**ORTHO or PARA**) on the ring.
- **DEACTIVATING GROUPS** or withdrawing groups attached to benzene ring can direct the incoming electrophile to specific position (**META**) on the ring.





EXCEPTION

Halides - *o,p* Directors / Deactivating

+R / -I / *o,p* / deactivating

-F
-Cl
-Br
-I

Halides represent a special case:

They are *o,p* directing groups that are deactivating

They are *o,p* directors (+R effect)

They are deactivating (-I effect)

- Other factors affecting aromatic electrophilic substitution include:

❑ Nature of the electrophile

❑ Presence and position of substituents on the aromatic ring

❑ Stability of the intermediate carbocation formed during the reaction

❑ Reaction conditions (solvent, temperature, catalyst).

Applications in Synthesis

Electrophilic substitution plays a vital role in **organic synthesis**. It is used to create pharmaceuticals, dyes, and polymers, showcasing its importance in both academic research and industrial applications.

Conclusion: The Art of Electrophilic Substitution

In conclusion, **electrophilic substitution** is an art that combines creativity with scientific rigor. By mastering this process, chemists can unlock the full potential of aromatic compounds, paving the way for innovative solutions in chemistry.