

↳ Isotope effects → A difference in the rate of reaction due to a difference in the Isotope.

C-H bond → easily break than C-D

C-D → ,

C-T → ,

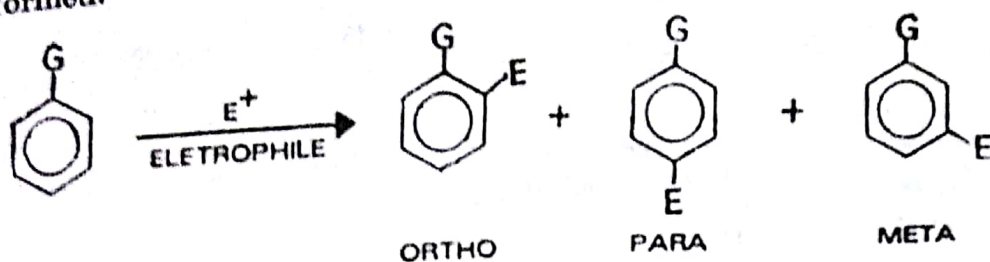
↳ ^{उदाहरण} Since H का lost reaction के rate-determining step में होता है Then H को D से replace करने पर reaction isotope effect दिखायेगी।

↳ Mostly में यह observe नहीं होता है but rate में nitration में होता है

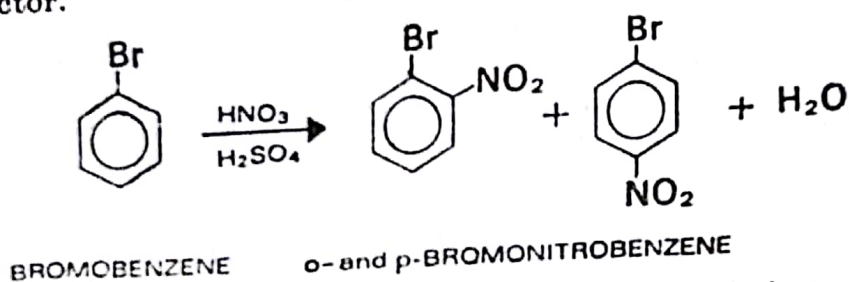
↳ Nitration → not show i.e. C₆H₆ & C₆D₆ की rate of nitration same

Points to Remember

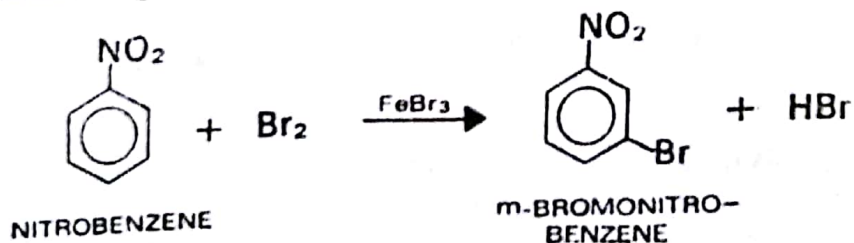
1. Substituted benzenes also undergo electrophilic substitution. There are three possible products that can form when a second substituent is introduced. Experimentally, one or two of the isomers are preferentially formed.



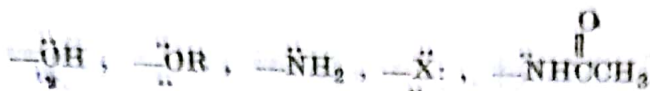
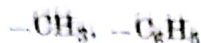
2. The substituent (G) already present on the ring determines where further substitution occurs. It also affects the rate at which substitution occurs.
3. **Ortho, Para Director.** A substituent that directs an incoming group to the ortho and para position is called an ortho, para director (**o,p-director**). For example, nitration of bromobenzene gives a mixture of *o*-bromonitrobenzene + *p*-bromonitrobenzene because the bromo group is an *o,p*-director.



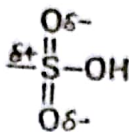
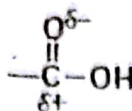
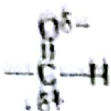
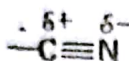
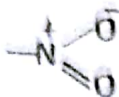
4. **Meta Director.** A substituent that directs an incoming group to the meta position is called a meta director (**m-director**). For example, bromination of nitrobenzene gives *m*-bromonitrobenzene because the nitro group on the ring is a *m*-director.



5. **Activating Group.** A substituent that makes benzene ring more reactive toward electrophilic substitution than benzene itself is called *activating group*.
6. **Deactivating Group.** A substituent that makes benzene ring less reactive toward electrophilic substitution than benzene itself is called *deactivating group*.
7. **Examples of o,p-Directors.** Alkyl groups, phenyl group, and substituents which have one or more nonbonding electron pairs (lone pairs) on the atom adjacent to the ring are o,p-directors.



8. **Examples of m-Directors.** Substituents which have a positive (or partial positive) charge on the atom adjacent to the ring are m-directors.



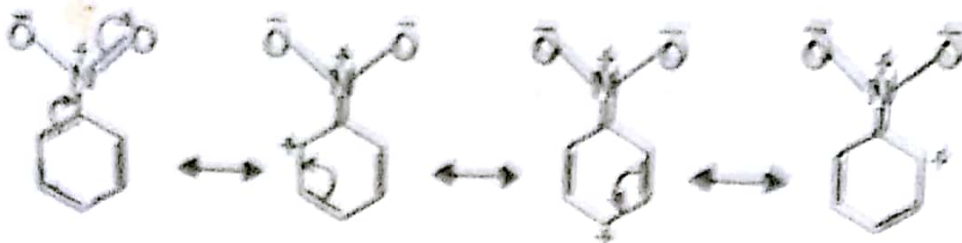
9. All o,p-directors are ring activating groups. Halogens are exceptions. They are o,p-directors but deactivating.
10. All m-directors are ring deactivating groups.

Meta Directors

Question 1. Explain why the nitro group ($-\text{NO}_2$) acts as a meta director and deactivating when it is present on a benzene ring undergoing electrophilic substitution.

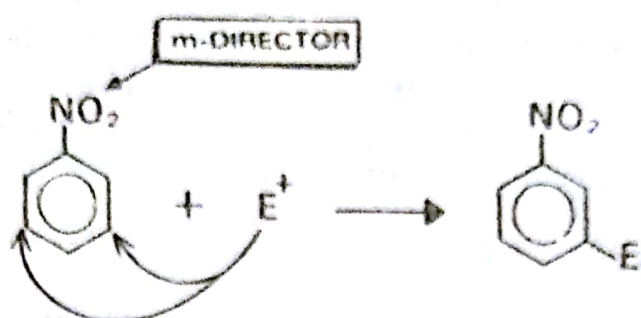
(Annamalai BSc, 1989; Assisi BSc, 1989; Bunsen BSc, 1989; Calicut BSc, 1989; Gachhad BSc, 1989; Kashiwa BSc, 1989; Kashiwa BSc, 1989; Panjab BSc, 1989; Punjab BSc, 1989; Punjab BSc, 1989; Shivaji BSc, 1981; M. S. University BSc, 1981; Annamalai BSc, 1982; Bombay BSc, 1982; Guen N. Univ BSc, 1982; IIT BSc, 1982; Madras BSc, 1982; Rajasthan BSc, 1982)

ANSWER. Nitrobenzene can be represented as a hybrid of the following resonance structures :



Why $-\text{NO}_2$ Group is Meta Director? Notice that the ortho and para positions in the above resonance structures carry a positive charge. An electrophile (E^+) cannot attack these positions (Like charges repel). It will attack the meta positions which are

relatively electron-rich. Thus, the nitro group directs all electrophiles to the meta positions.



Why $-\text{NO}_2$ Group is Deactivating? (Reminder: The $-\text{NO}_2$ group is deactivating. This means that nitrobenzene undergoes electrophilic substitution more slowly than benzene). Notice that the nitro group withdraws electrons from the ring by resonance. It decreases electron density of the ring and makes it less attractive to an incoming electrophile. Thus, the electrophilic substitution is slow, and requires vigorous reagents and conditions.

Question 2. Explain why nitrobenzene undergoes electrophilic substitution more slowly than benzene.