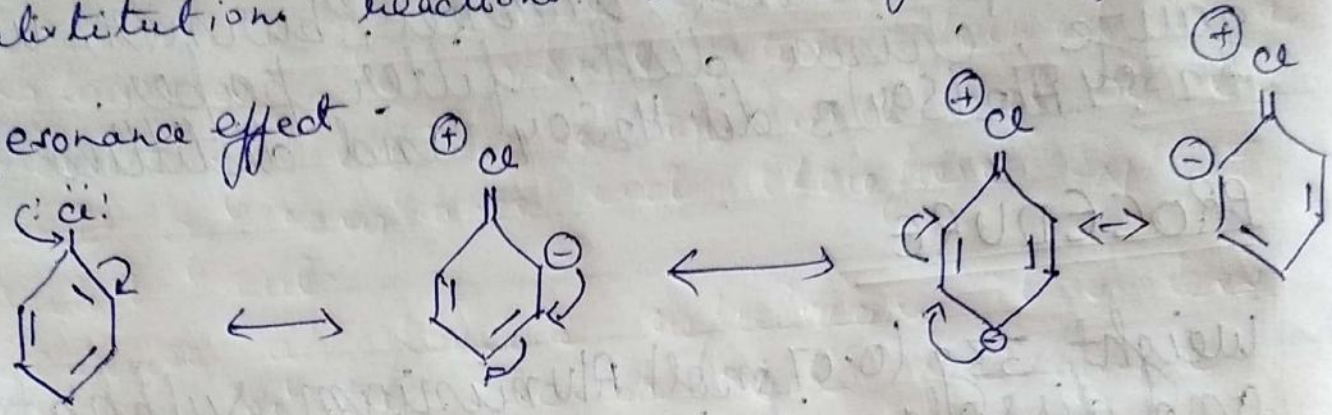
1.6. Chemical reactions of Haloarenes:

a) Nucleophilic substitution reaction- Aryl halides are less reactive towards nucleophilic substitution reactions due to following reasons.

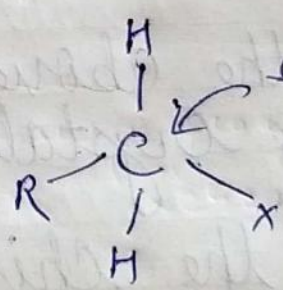
i) Resonance effect.



Due to resonance C-Cl acquires a partial double bond character which causes difficulty in bond cleavage so they are less reactive towards nucleophilic substitution reaction.

ii) Difference in hybridisation of carbon atom in C-X bond

Haloarene



Haloalkane

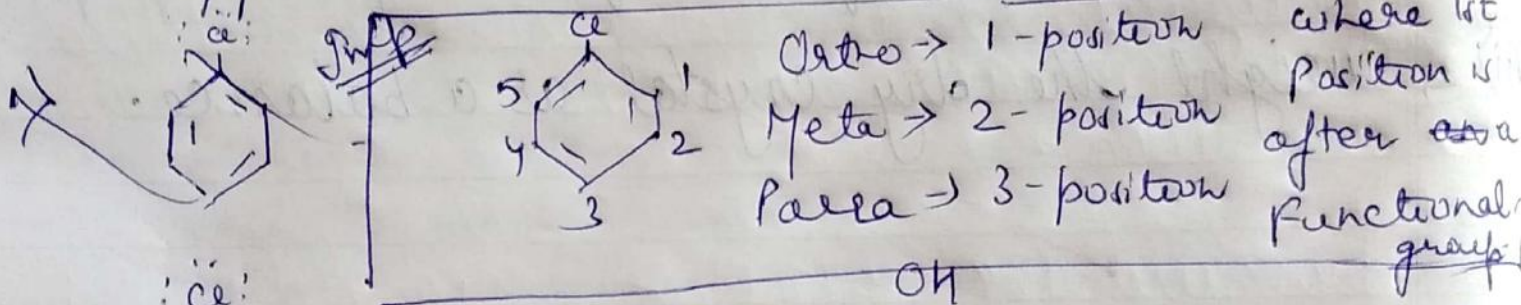
sp^2 hybridised carbon - greater s-character - more electronegative - 169 pm

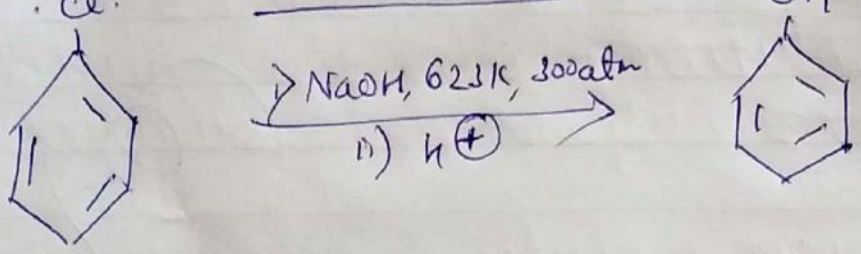
sp^3 hybridised carbon - less s-character - 177 pm

Since it is difficult to break a shorter bond than a longer bond so haloarenes are less reactive than haloalkane towards nucleophilic substitution reaction.

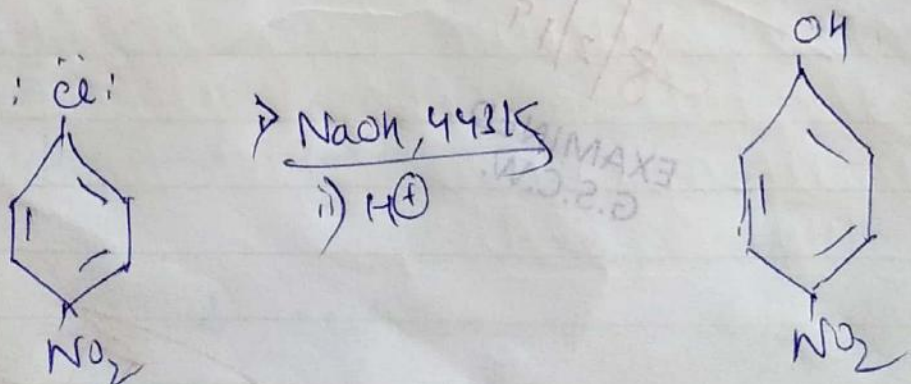
iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 is ruled out.

iv) Because of repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.



1) 

2) Presence of Electron withdrawing groups ($-NO_2$) at Ortho and para position increases reactivity of haloarenes.



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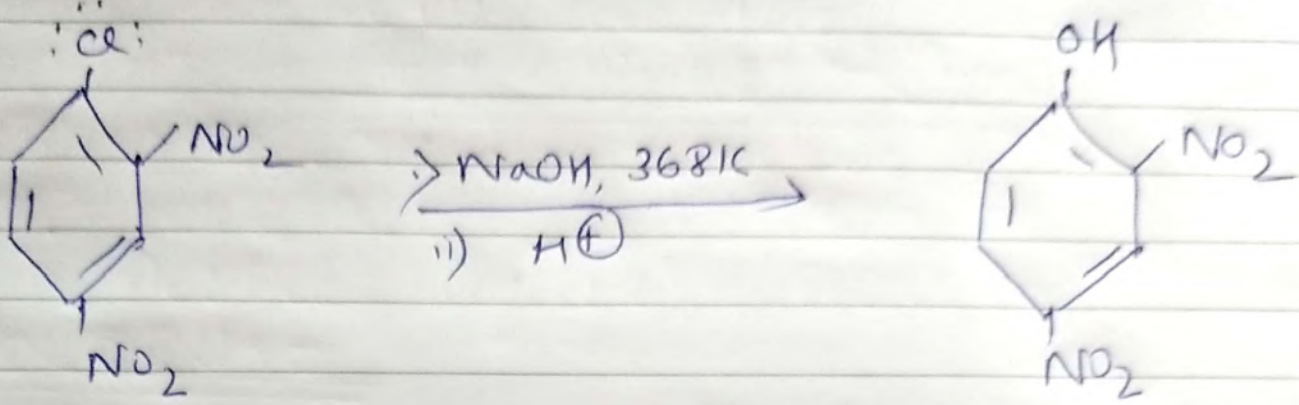

Ortho and para position substituents effect is more pronounced as compared to meta-position.