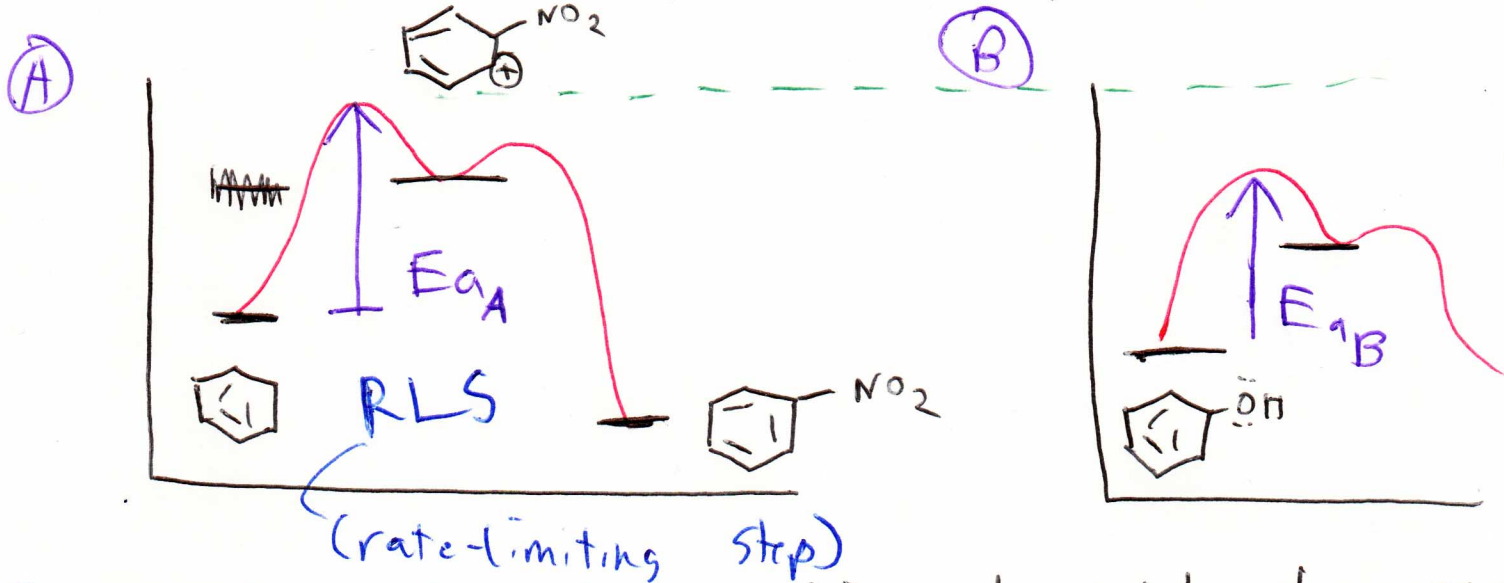
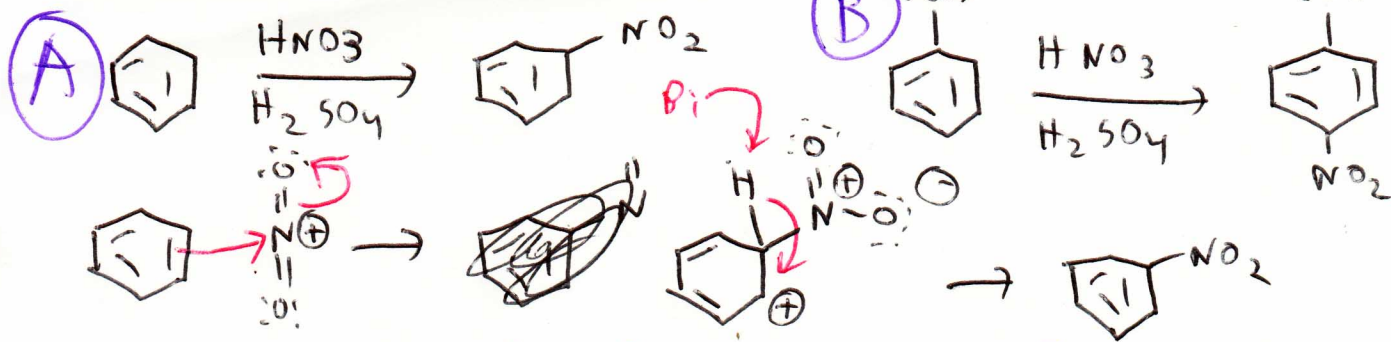


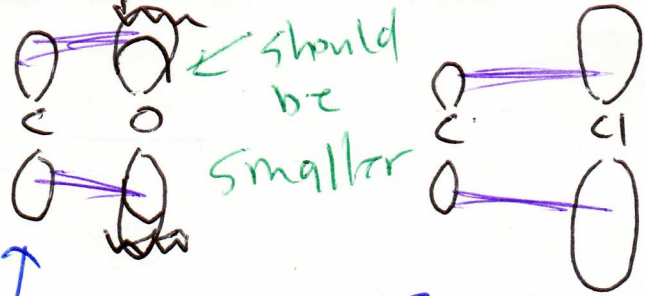
3/12/12



Due to the electron density being donated by the  $-\text{OH}$  on phenol, the activation energy to reach the intermediate ( $E_{aB}$ ) is lower than in the similar reaction with unsubstituted benzene ( $E_{aA}$ ), since the electron density from phenol is helping to delocalize the carbocation formed & make the attack on the electrophile easier.

Lower  $E_a \rightarrow$  higher rate  $\rightarrow$  activation

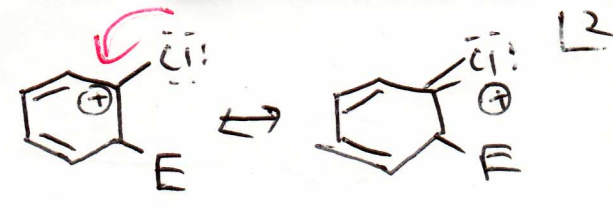
- Even though oxygen is electronegative and will withdraw  $e^-$  density by induction, it also has good orbital overlap w/ carbon, and it provides more  $e^-$  density through delocalization than it withdraws by induction.



better overlap  
(similar in size)

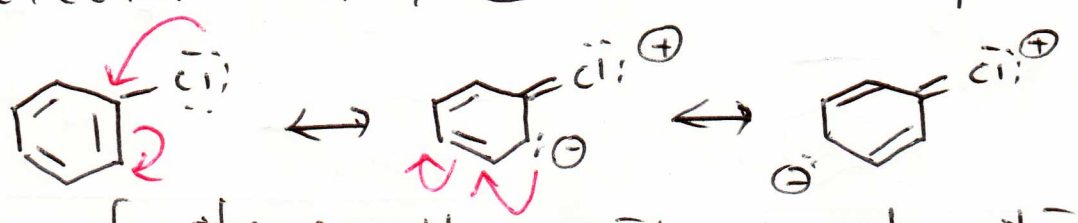
poorer overlap  
due to mismatch in orbital size

Cl has larger orbitals



Halogens are o,p-directors but are deactivators

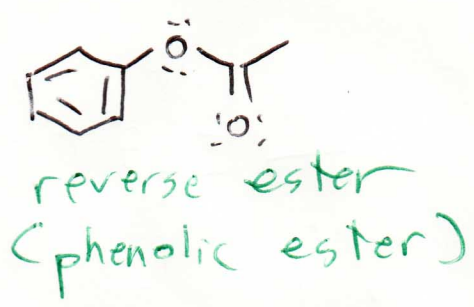
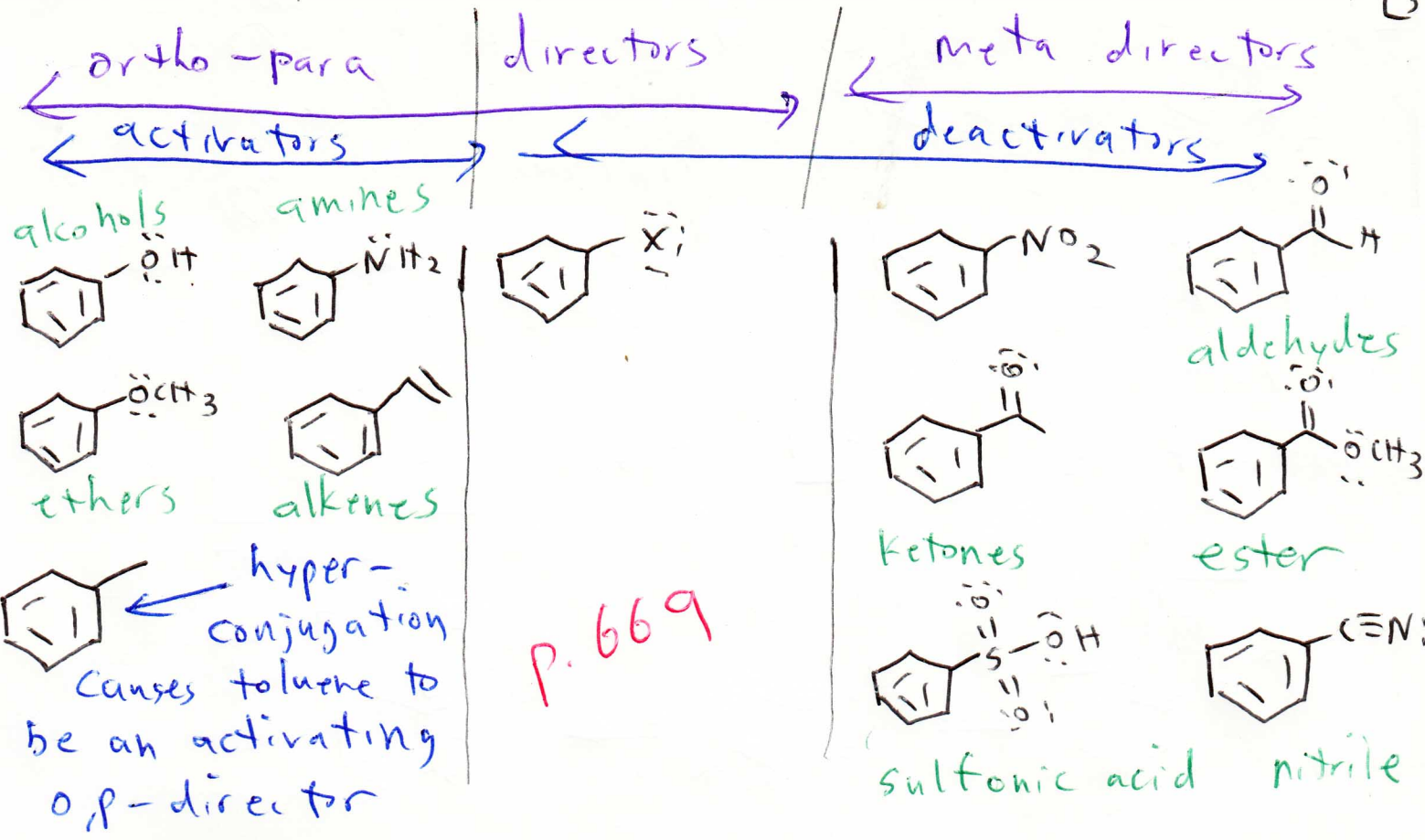
Resonance involving the halogen will always put more electron density @ the ortho + para positions,



Regardless of the overall activating or deactivating effect of the halogen,

Cl, Br, I → Since these halogens are larger than carbon, they have poorer orbital overlap, so they do not provide as much e<sup>-</sup> density through resonance as they ~~do~~ withdraw by induction, so they are deactivators.

F → Fluorine is similar in size to carbon so it has good orbital overlap, but it is the most electro-negative element, so it withdraws more e<sup>-</sup> density than it donates, so it is a deactivator



Frontier orbital theory → Pericyclic rxn

