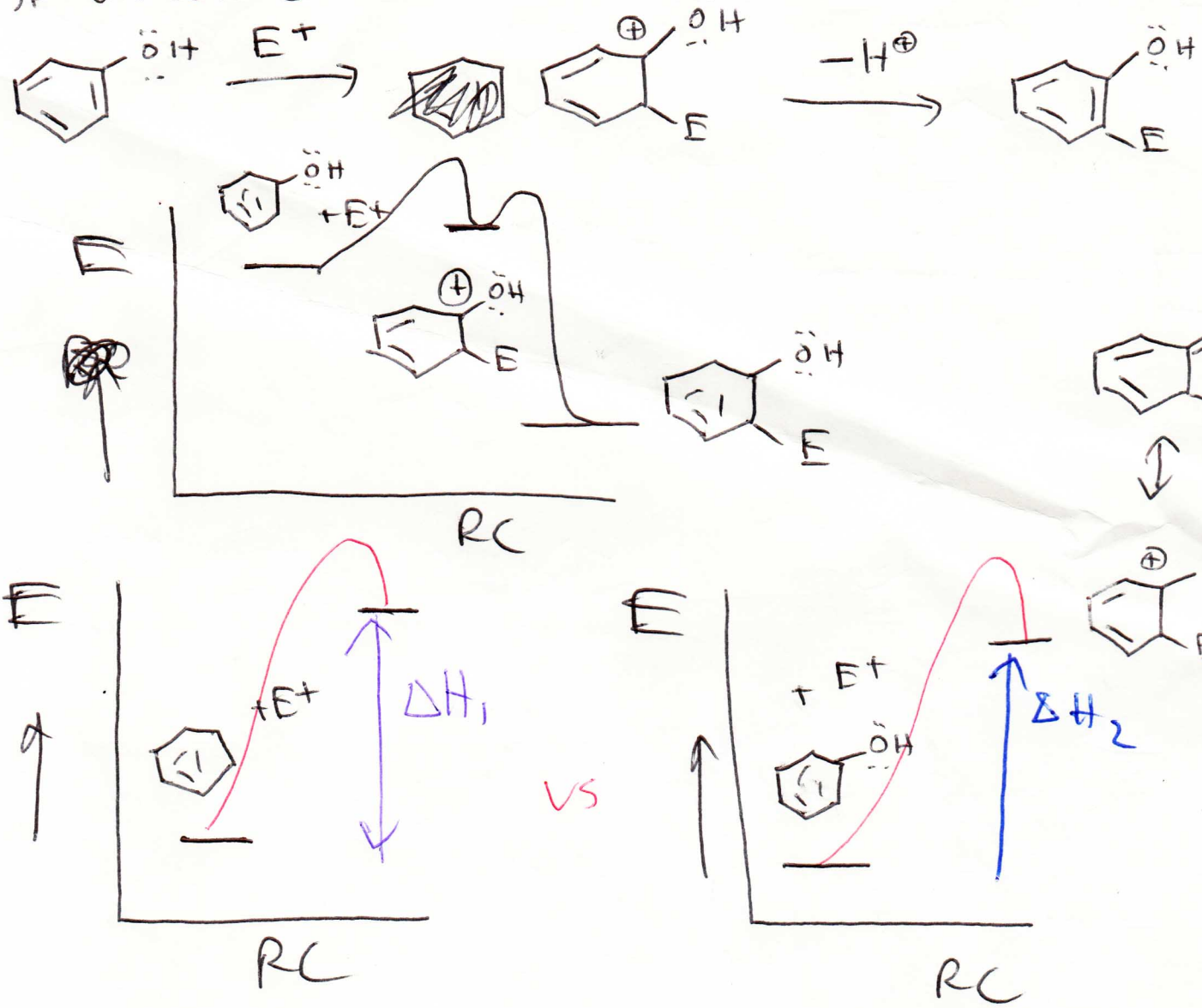
o,p-directors



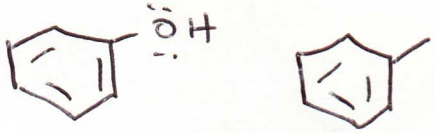




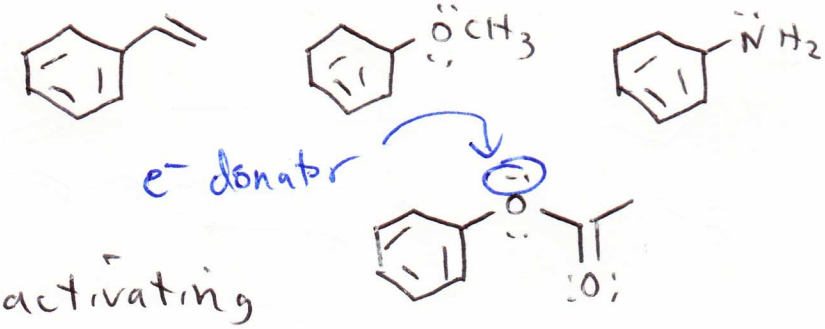
$\Delta H_1 > \Delta H_2$

The formation of an arenium ( ) is the rate-limiting step in electrophilic aromatic substitution. Any factor that would stabilize the intermediate (the arenium ion) would also cause a lower $E_a$ to reach that intermediate, which increases the rate of rxn.

Since o,p-directors help stabilize an arenium ion by providing electron density by resonance, they undergo faster electrophilic aromatic substitution.



(due to hyperconjugation)

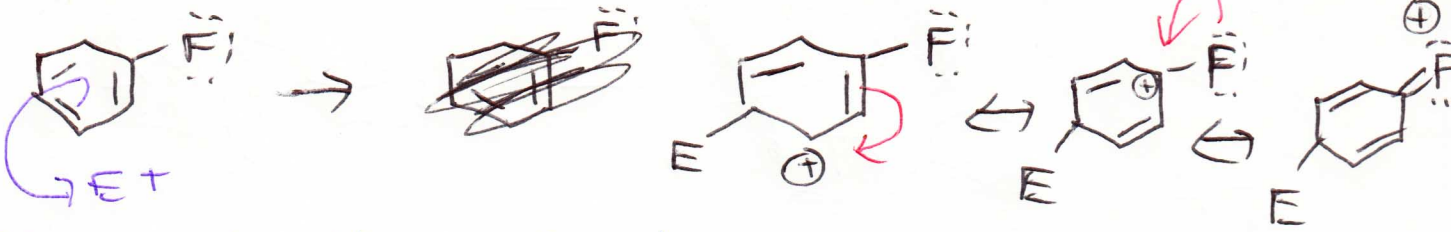



directing vs. activating

Although oxygen is very electronegative and can withdraw electron density by induction, it also has very good orbital overlap w/ carbon, the ability of oxygen to share e⁻ density via conjugation/resonance is greater than its tendency to remove e⁻ density by induction, so oxygen is an activator,

Although fluorine can participate in delocalization, it withdraws more e⁻ density by induction than it provides through resonance ⟶ deactivator.

(d. withdrawing e⁻ density raises the energy of the arenium ion, which means forming the ion requires greater Ea, so the rate is lower),

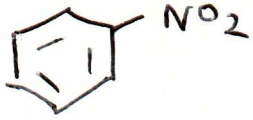
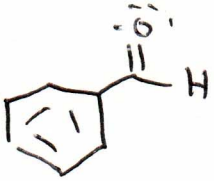
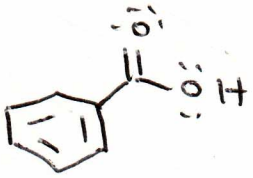
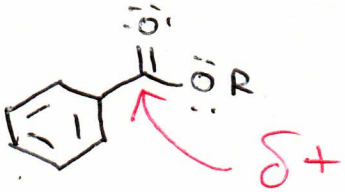



Fluorine is still an o,p-director since it can delocalize the ⊕ charge formed.

Chlorine (and Bromine + iodine) has poorer orbital overlap w/ carbon, so it cannot provide as much e⁻ density through delocalization as it withdraws due to induction ⟶

o,p- deactivators,

Meta directors

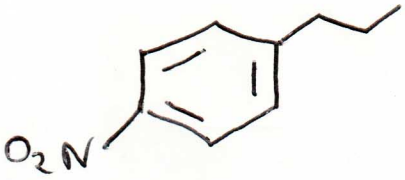






o,p – directors

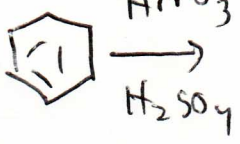
meta-directors

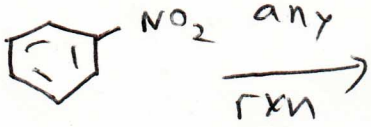
| activators | deactivators | nitro, aldehydes, |
|---|---|---|
| alkyl, alkene, alkynes, | halogens | ketones, |
| alcohols, ethers, thiols | | carboxylic acid |
| amines, "rerverse" esters | | derivatives, |

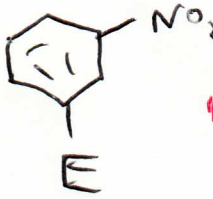
Synthesis




from 




meta

Must perform nitration last!