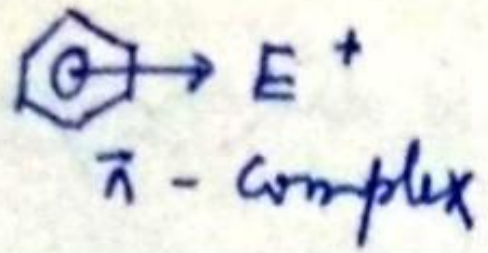


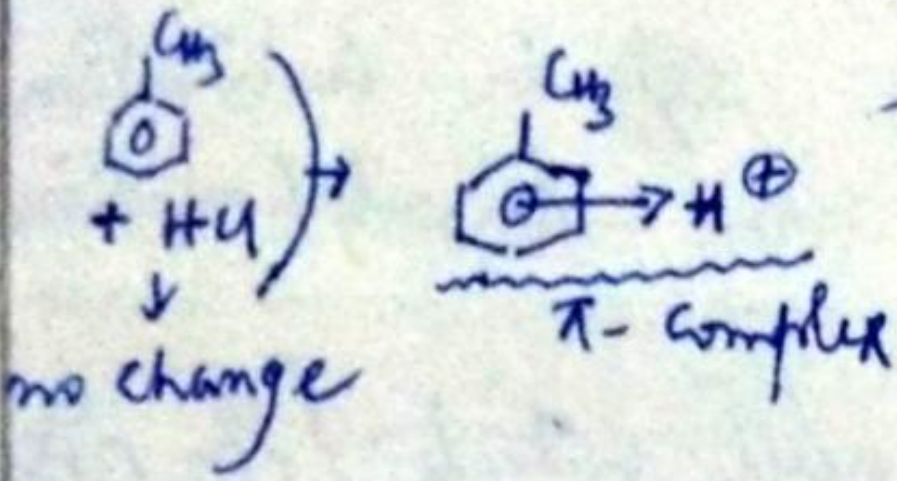
π - and σ - Complexes

π - Complex

Ref: P. Sykes (Organic)

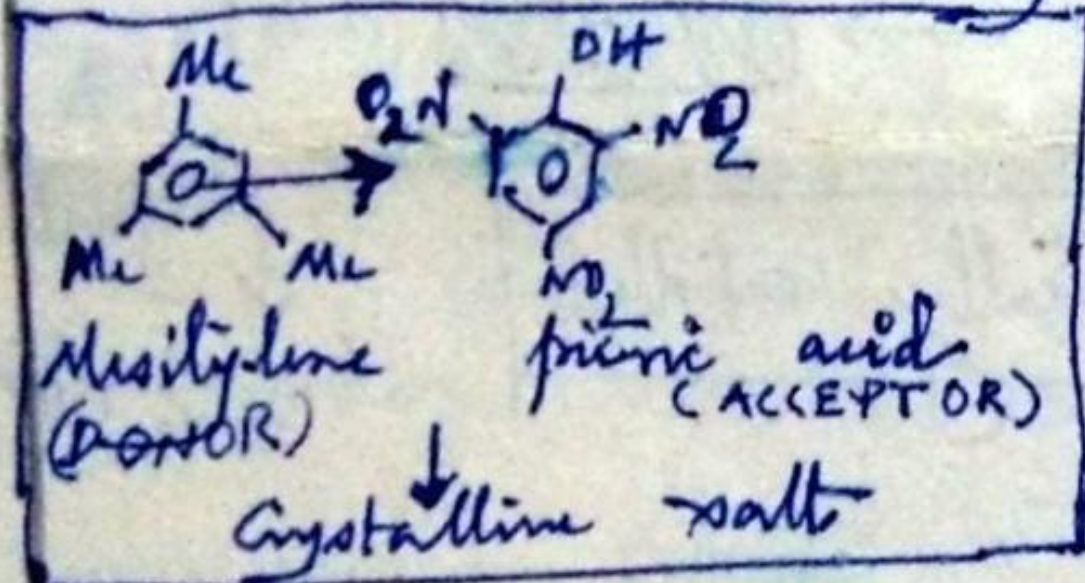


an interaction between π-cloud of benzene ring and electrophile



π e⁻ cloud as a whole interacts with vacant orbital of H⁺.
No actual C-H bond formation takes place at this stage is proved by the fact if the reaction is repeated with DCl at -78°C, no D-incorporation takes place.

When mesitylene is treated with picric acid, a crystalline salt results which is named as charge transfer complex a type of π-complex.

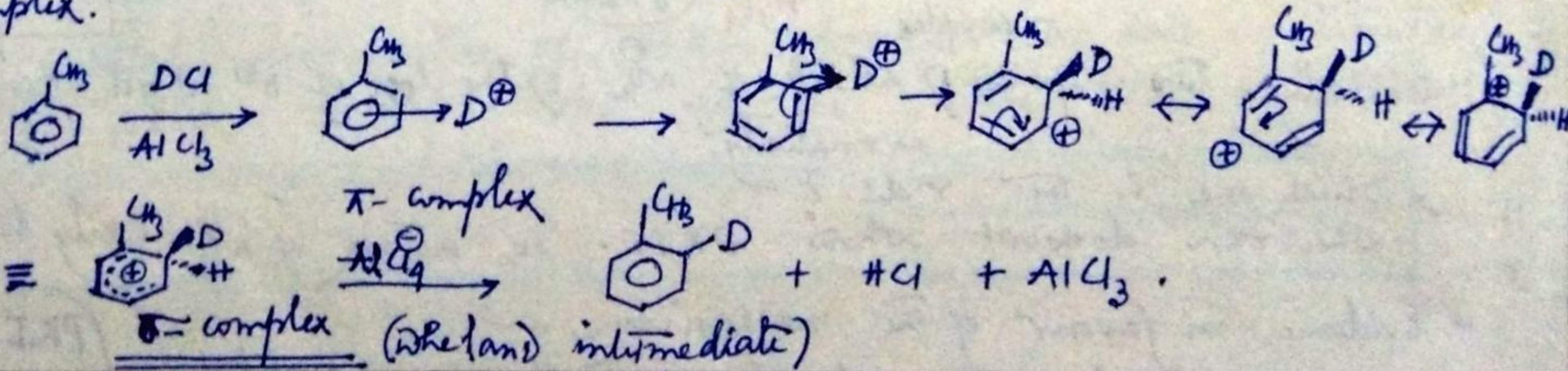


CHARGE TRANSFER COMPLEX

Here mesitylene acts as a donor (π-excess) and picric acid acts as an acceptor (π-deficient).

σ - Complex

If the reaction of toluene with DCl is repeated in the presence of AlCl₃, D-incorporation does take place → indicating the actual C-D bond formation. Solⁿ becomes intensely colored. This results the formation of a new complex, known as σ-complex.



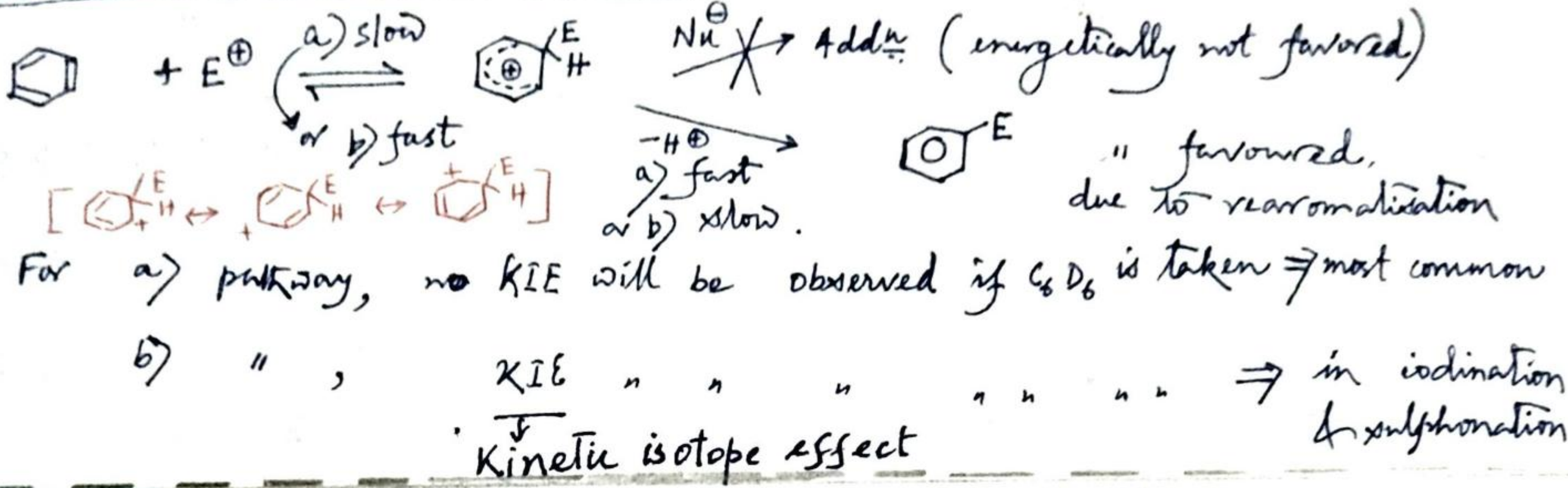
Differences between π - and σ - complexes

- π - complex
- i) no actual bond formation
 - ii) no change in colour of the solution
 - iii) no appreciable change in UV spectra
 - iv) no change in conductivity.

- σ - complex
- i) actual bond formation.
 - ii) The solution becomes intensely coloured.
 - iii) appreciable change in UV spectra
 - iv) change in conductivity.

SEAr \Rightarrow Electrophilic Aromatic Substitution

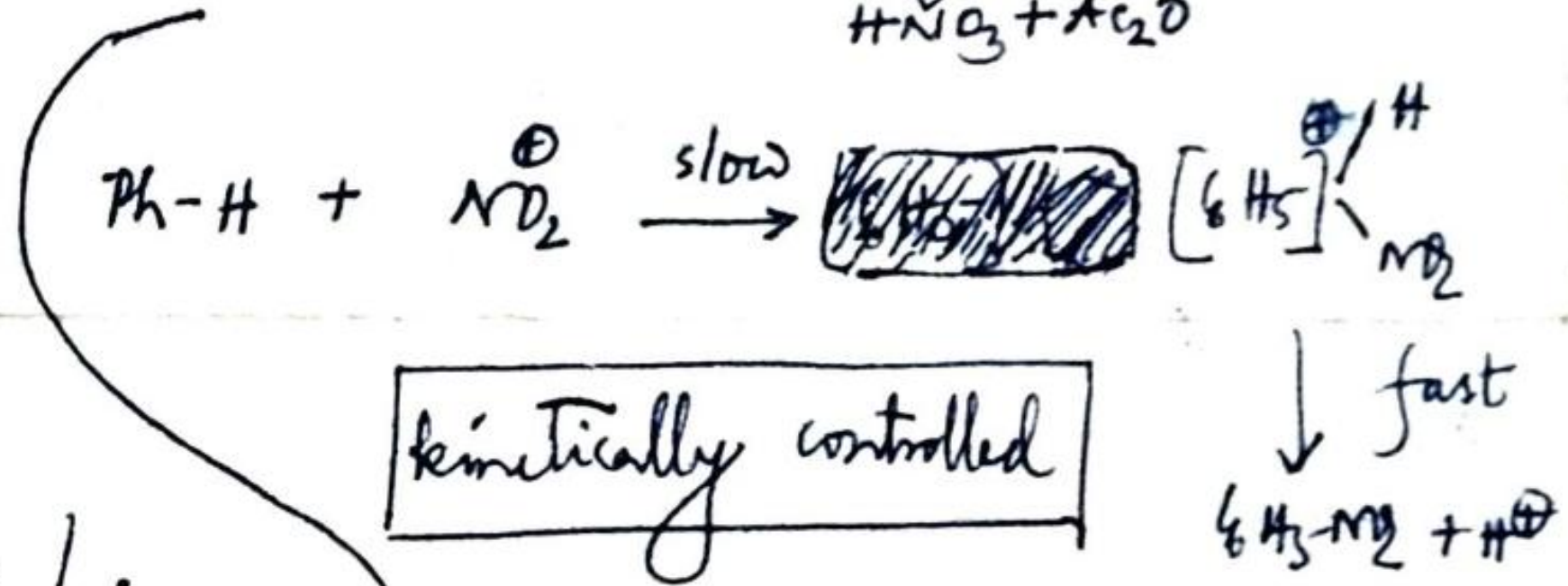
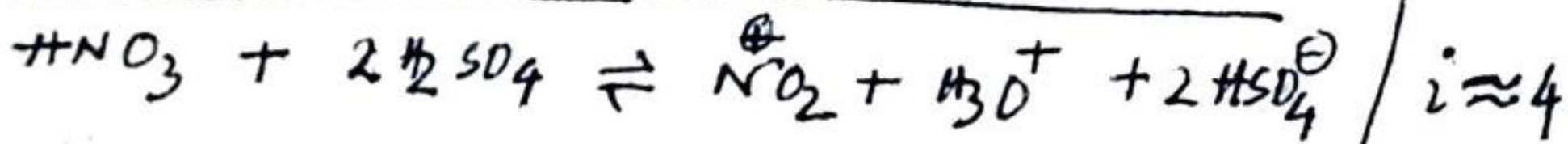
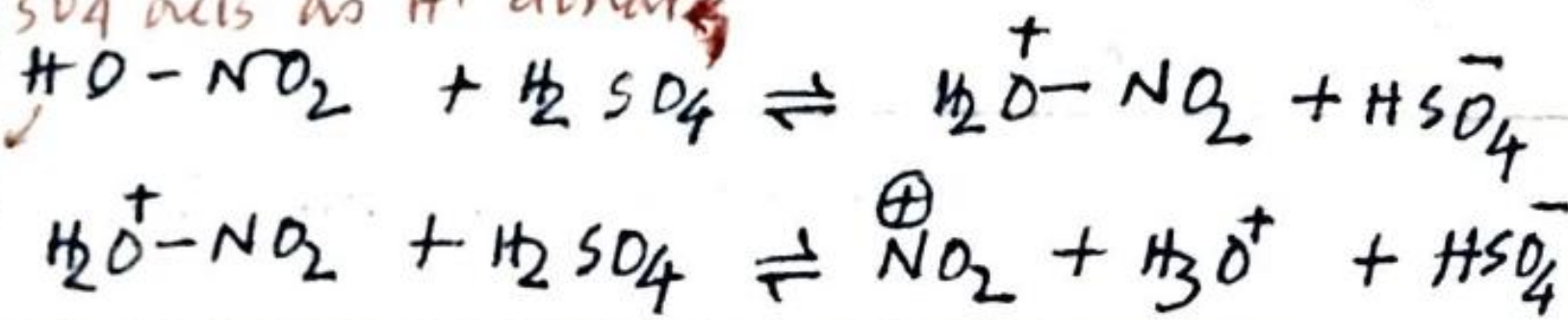
Mechanism of SEAr rxn. (bimolecular):



- Nitration: by mixed acid / fuming ac. or dil. HNO_3 / N_2O_5 / acyl nitrate / $NO_2^+ BF_4^-$.
 1:1 $C.HNO_3 + H_2SO_4$

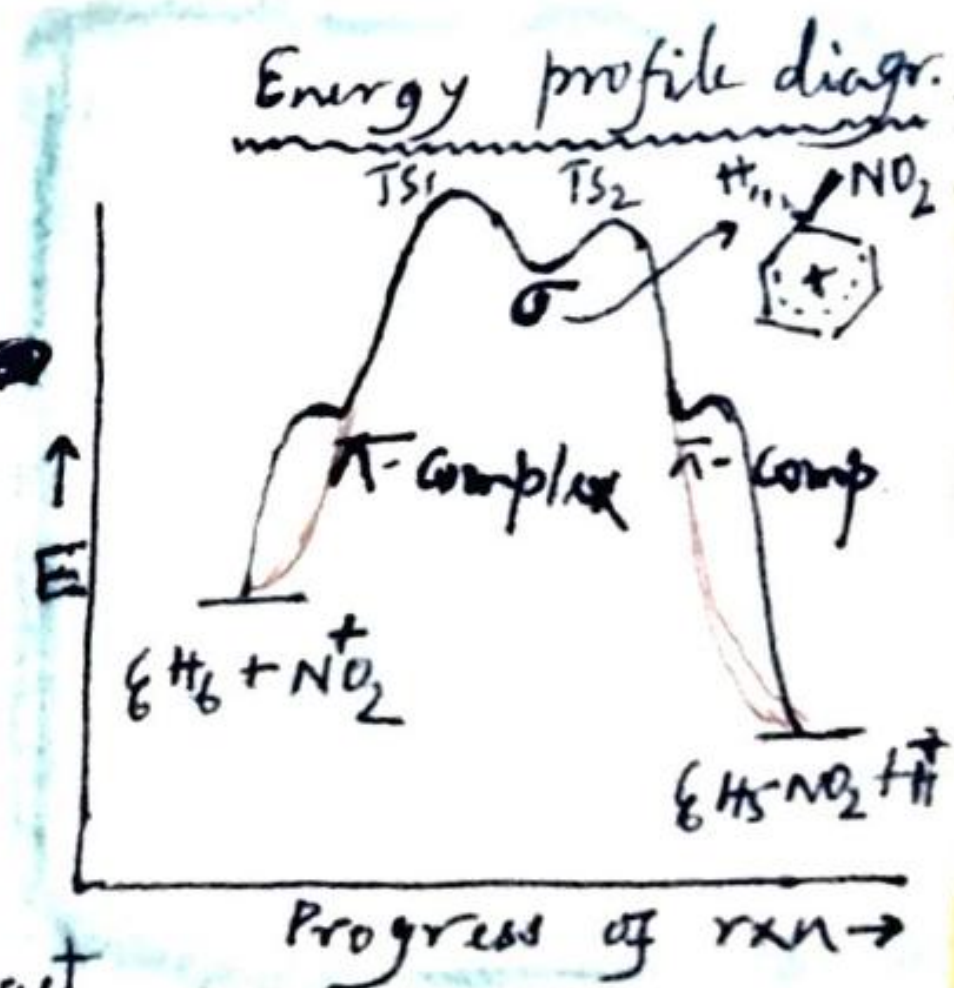
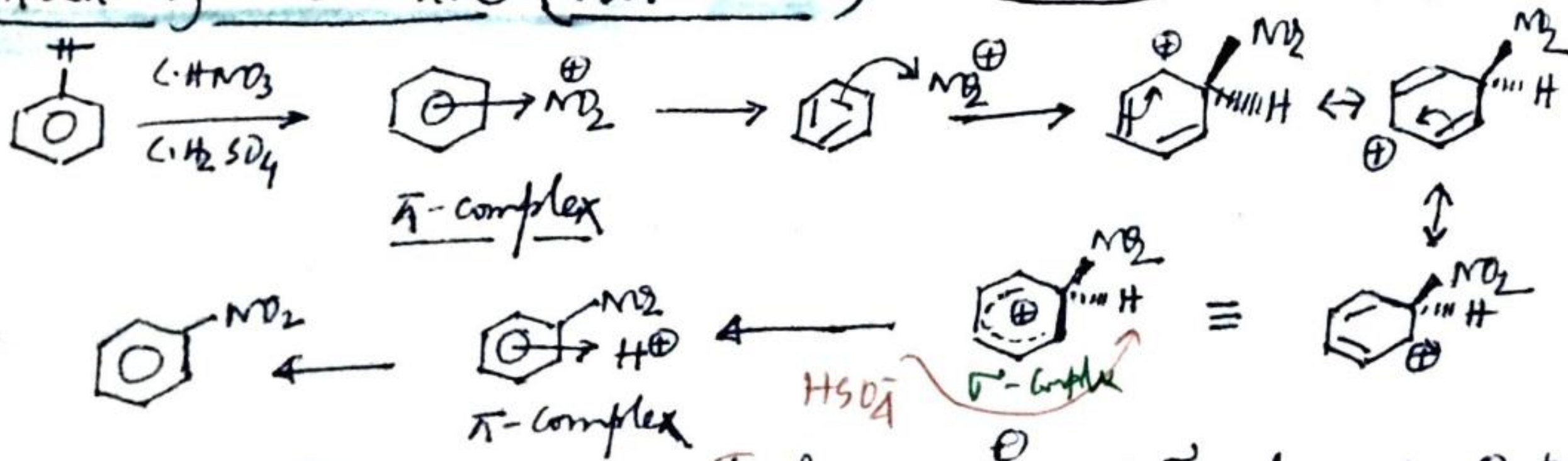
Mixed acid \Rightarrow 1:1 $C.HNO_3 + H_2SO_4$

$C.H_2SO_4$ acts as H^+ donor
 acts as base



Mech. of the rxn (nitration):

Nitration Benzene



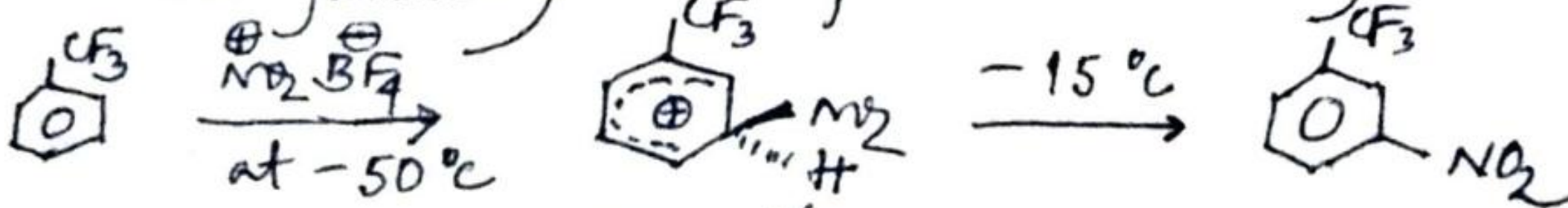
Basically two steps \Rightarrow 1) attack of NO_2^+ 2) The loss of H^+ to get aromaticity.

Which one is the rds.?

The rxn does not show PKIE. So, attack of NO_2^+ likely to be the rds.

Evidence in favour of the mechanism —

The following σ -complex has actually been isolated.



σ -complex (isolated)

Actually, the σ -complex ~~can be~~ isolated.

PKIE \Rightarrow Primary Kinetic Isotope Effect