Aromatic Electrophilic Substitution

3rd Sem
Lecture – 1
Paper- CC7

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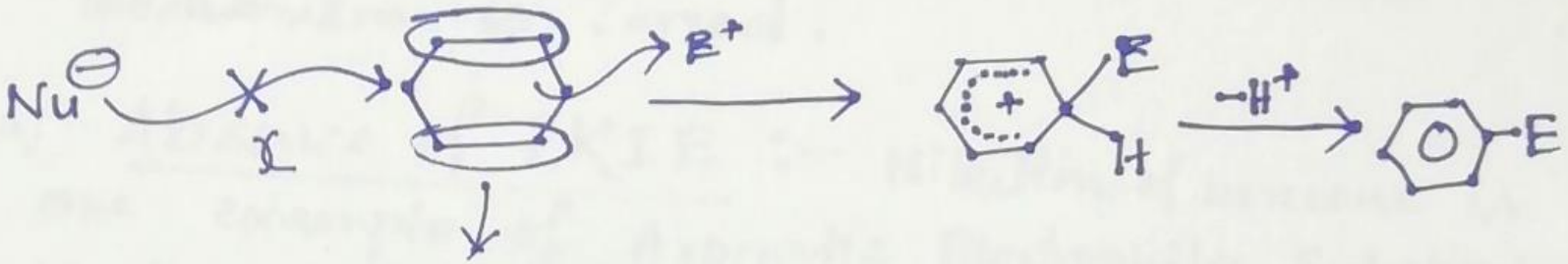
Aromatic Electrophilic Substitution

S-1

Aromatic Electrophilic Substitution



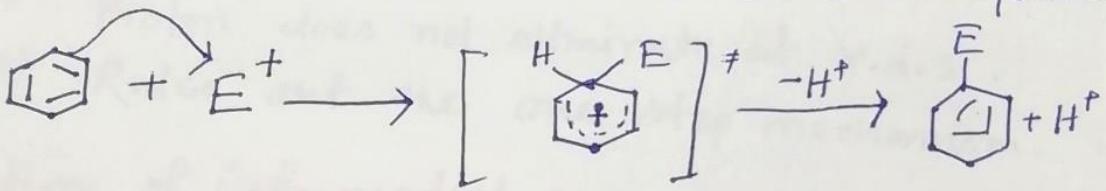
act as Nu^-

due to π electrons cloud above and below the benzene ring its attracts E^+ strongly.

Aromatic Electrophilic Substitution

Mechanism :- reacⁿ may take place in the two different ways.

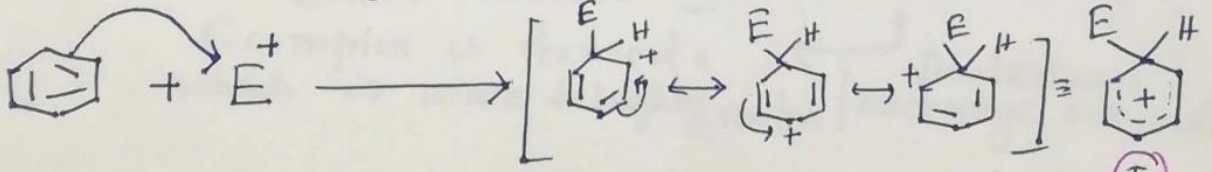
(i) **Concerted Process** :- By direct displacement → C–H bond is broken and C–E bond is formed



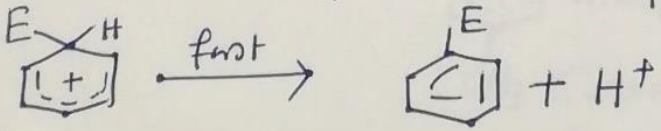
T.S

(ii) **Two step Process** :-

1st step :- involve E^+ attack on the aromatic ring → forming resonance stabilised carbocation (I)



2nd step :- Fast step → eliminate a proton σ-complex

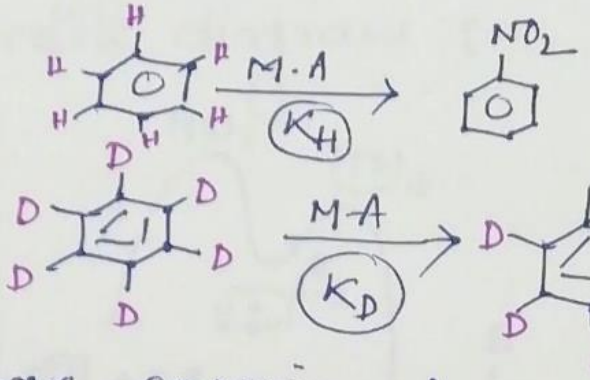


Aromatic Electrophilic Substitution

Sol Which of the above two process is correct ??

⇒ Following two observation show that 2nd mechanism is correct.

a) Absence of PKIE :- Nitration of benzene is one example of Aromatic Electrophilic Substitution reacⁿ. The rates of nitration of benzene, deuterio and tritio benzene are same.



$K_H = K_D$

i.e $\frac{K_H}{K_D} = 1$

⇒ Above experiment convince that →

(i) The mechanism is two step

(ii) Proton does not eliminate at r.d.s.

(iii) Rules out the one step mechanism.

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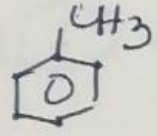
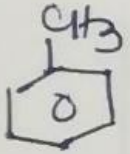
(b) Isolation of intermediate :-

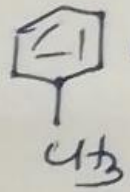


+ $AlCl_3$ ⟶ No reacⁿ



+ $AlCl_3$ + HCl ⟶ (−78°C) Green colour soln which conduct electricity ?

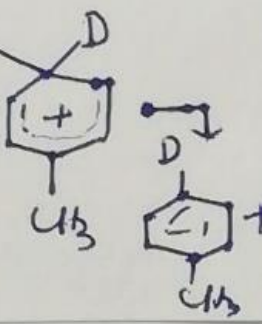
which indicate a σ-complex is formed which is ionic & highly reactive ⟵ Deuterium exchange take pl



+ $AlCl_3$ + HCl ⟶

σ-complex

$AlCl_4^{\ominus}$ ⟶ (DCl)



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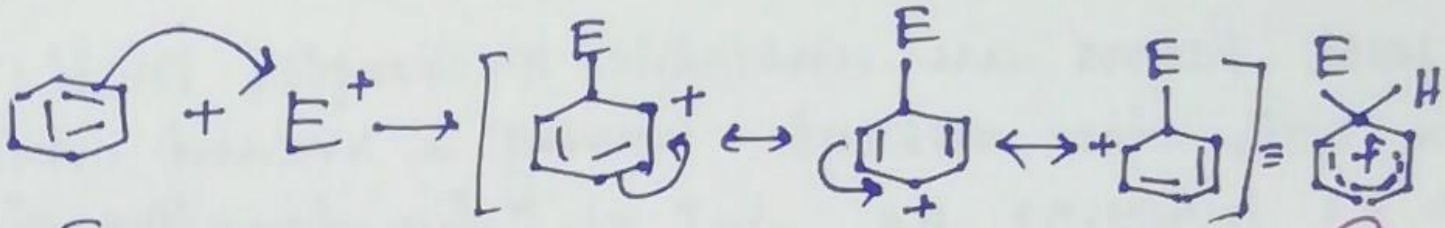
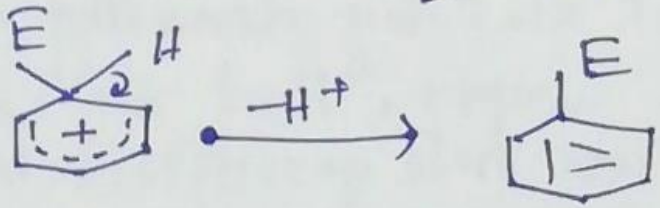
Therefore the actual mechanism is —

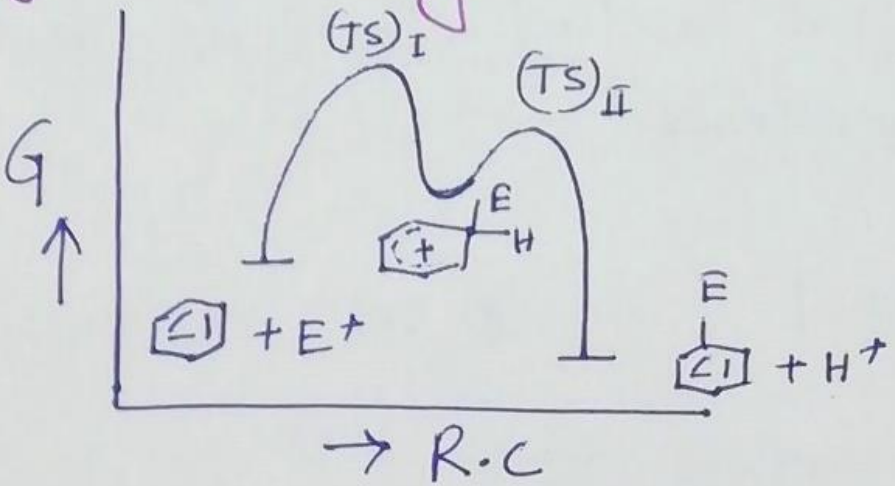
Step-I



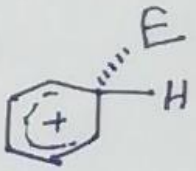
Step-II



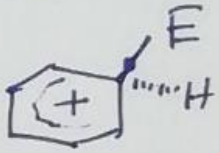
Energy Profile diagram :-



TS-I ⇒



(TS)II ⇒



1st step is R.D.S

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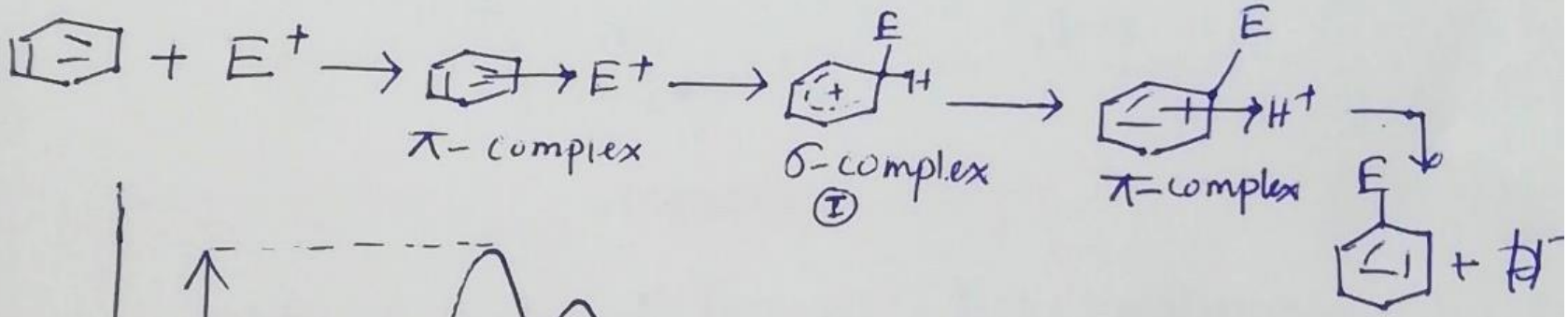
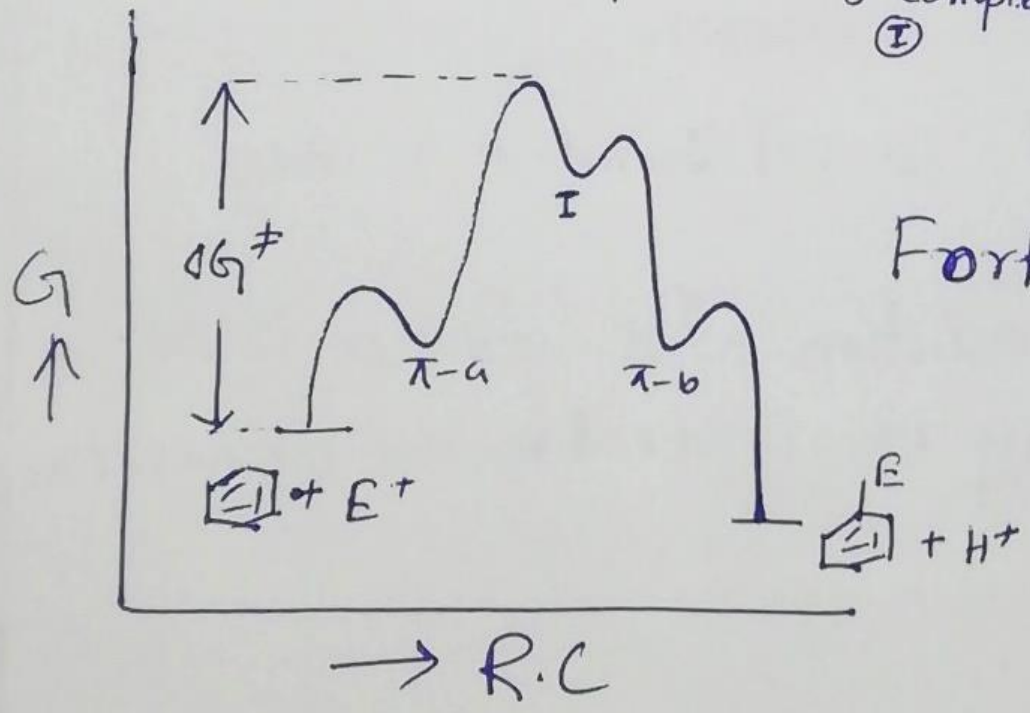
If we consider the formation π- complex → which is formed before forming σ- complex → then energy profile diagram of the process is —





Formation of σ- complex is r.d.s

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π- complex or Charge transfer Complex

Benzene forms an unstable π-complex in 1:1 molar ration with other molecule having a vacant orbital such as halogens, Hx, Ag^+ etc. by donating electrons which the other molecules accepts. But no covalent bond is formed, the two are held together by weak electrostatic attraction.

π-complex are colourless or coloured. They carry no formal charge and do not conduct electricity, much less stable than σ-complex

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example

I_2 in CCl_4 ⟶ violet ——① soln

 in CCl_4 ⟶ Colourless ——② soln

(1+2) soln mixer ⟶ brown colour ⟶ indicates the formation of π-complex

 + I—I $\xrightarrow{CCl_4}$ 

brown

> In π-complex E^+ is not bonded to any particular carbon.

> Formation and dissociation of π-complex is so fast/rapid that it may be ignored in the mechani