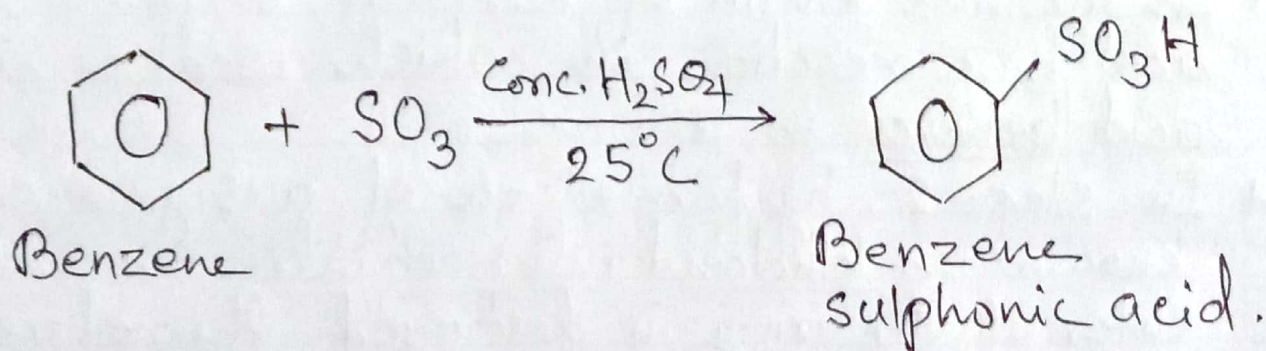


(2) Sulphonation - The replacement of H atom of benzene nucleus by  $-SO_3H$  group is called sulphonation and the product formed is called benzene sulphonic acid.

Sulphonation reaction is carried out in presence of any one of the following reagents

- i) Conc.  $H_2SO_4$
- ii) Chlorosulphonic acid -  $ClSO_3H$
- iii) Oleum -  $H_2S_2O_7$
- iv) Fuming sulphuric acid -  $(\text{conc. } H_2SO_4 + SO_3)$

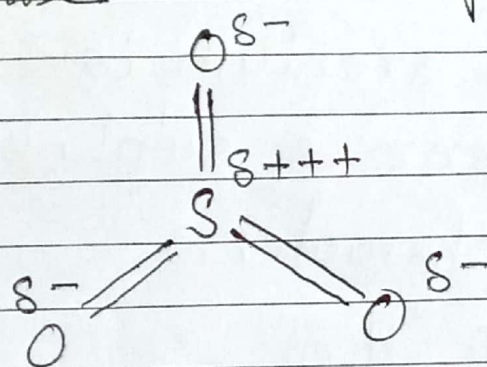
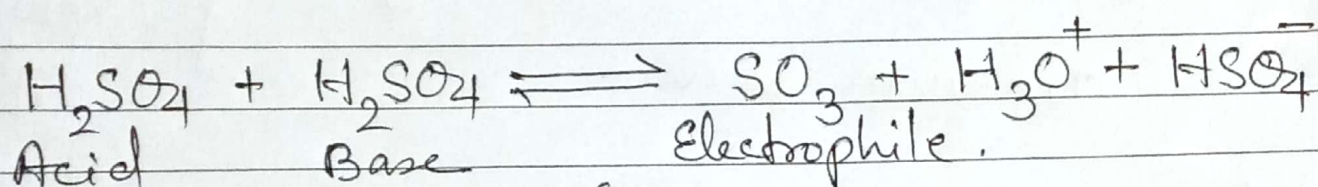
Fuming sulphuric acid is the concentrated sulphuric acid saturated with  $SO_3$  vapours. It reacts with benzene at room temperature and produces benzene sulphonic acid. In presence of concentrated sulphuric acid sulphonation reaction proceeds slowly.





Mechanism of sulphonation - Following steps are involved in the sulphonation reaction..

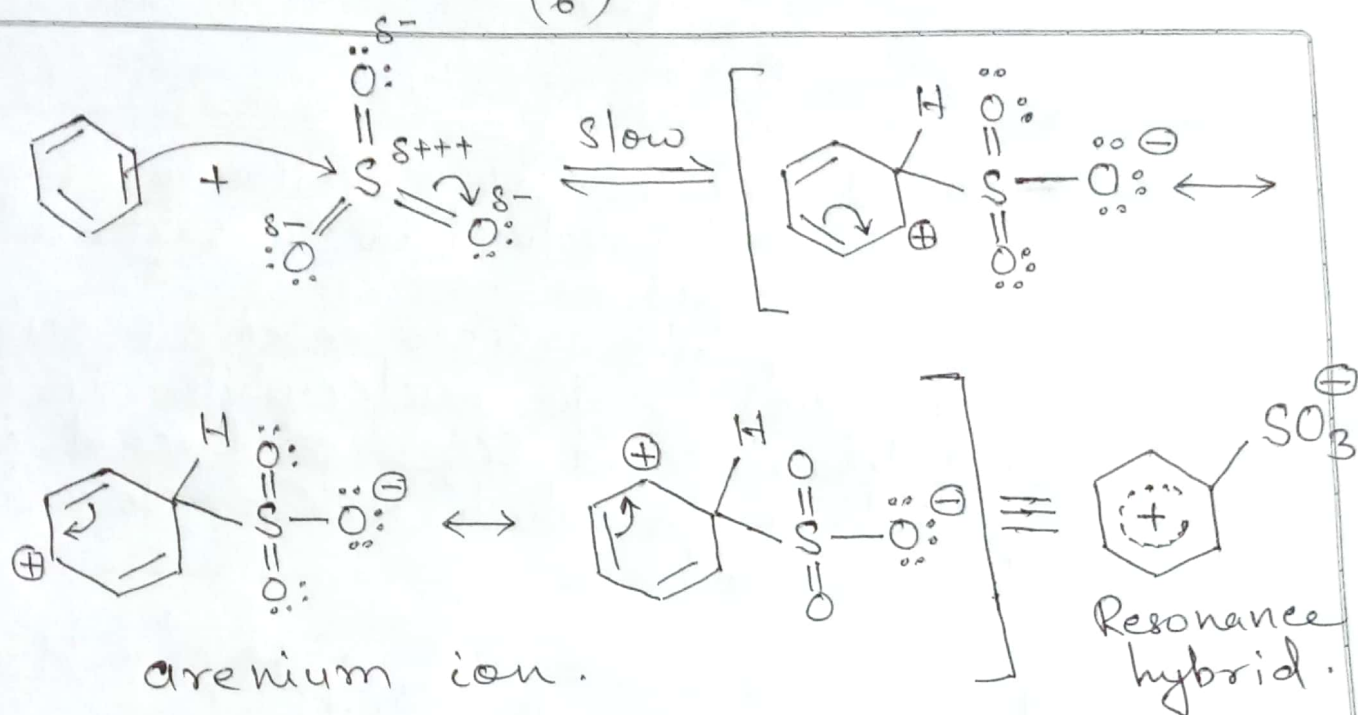
Step - 1 : In sulphonation reaction, Sulphur trioxide is the nucleophile. In concentrated sulphuric acid  $\text{SO}_3$  is produced in an equilibrium in which  $\text{H}_2\text{SO}_4$  acts as both an acid and a base



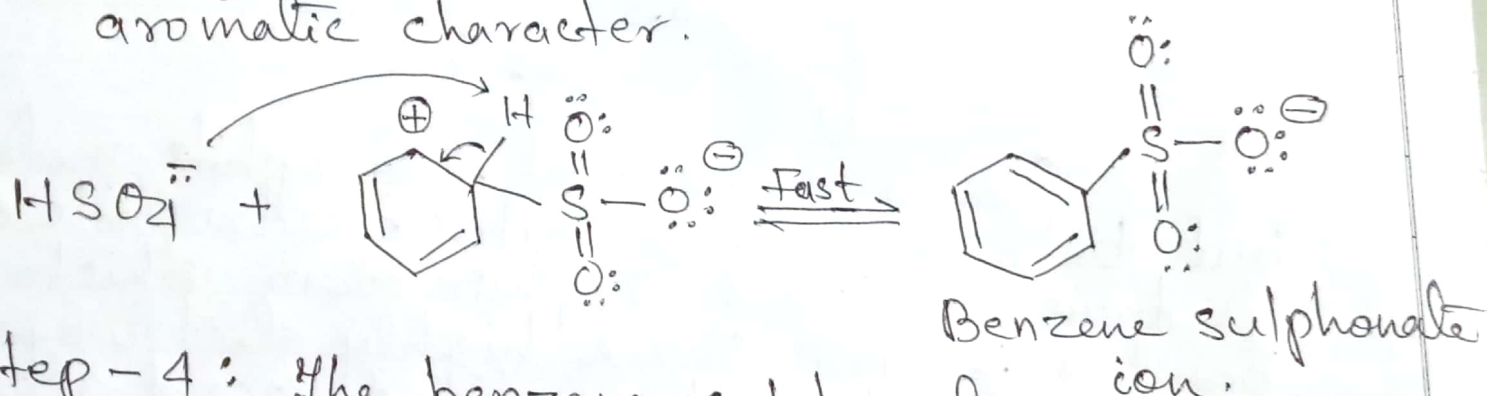
$\text{SO}_3$  is a neutral electrophile molecule but behaves as a powerful electrophile due to electron deficient sulfur atom which is bonded with three highly electronegative oxygen. Sulphur also contains vacant d-orbital hence it has high electron acceptor tendency.

Step - 2 : The electrophile  $\text{SO}_3$  accepts electron from  $\pi$ -bond of the aromatic carbon to form a sigma complex. It is slow and rate determining step.

(6)



Step - 3: The arenium ion loses a proton to form benzene sulphonate ion and retains aromatic character.



Step - 4: The benzene sulphonate ion accepts a proton from oxonium ion and gives benzene sulphonic acid.

