

D.B. College (Jaynagar) Lect 1-9

Akhilesh Kumar Singh

Chemistry department B.Sc(Hons) Part-I

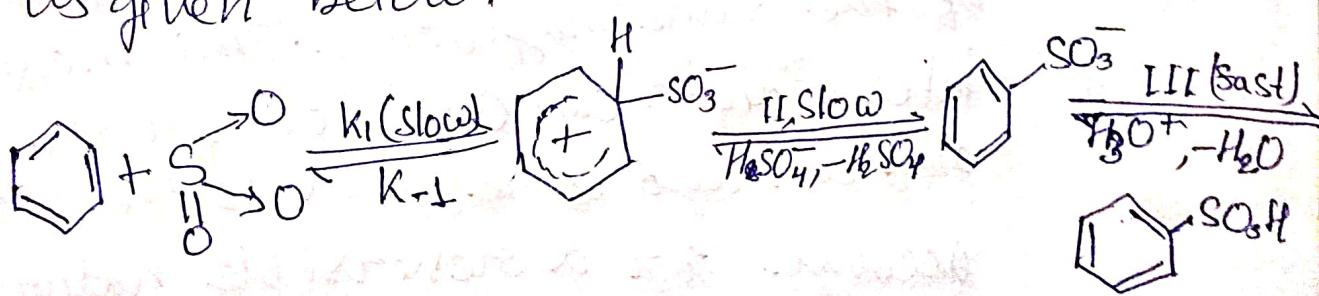
Mobl-8750390927

### (3) Sulphonation

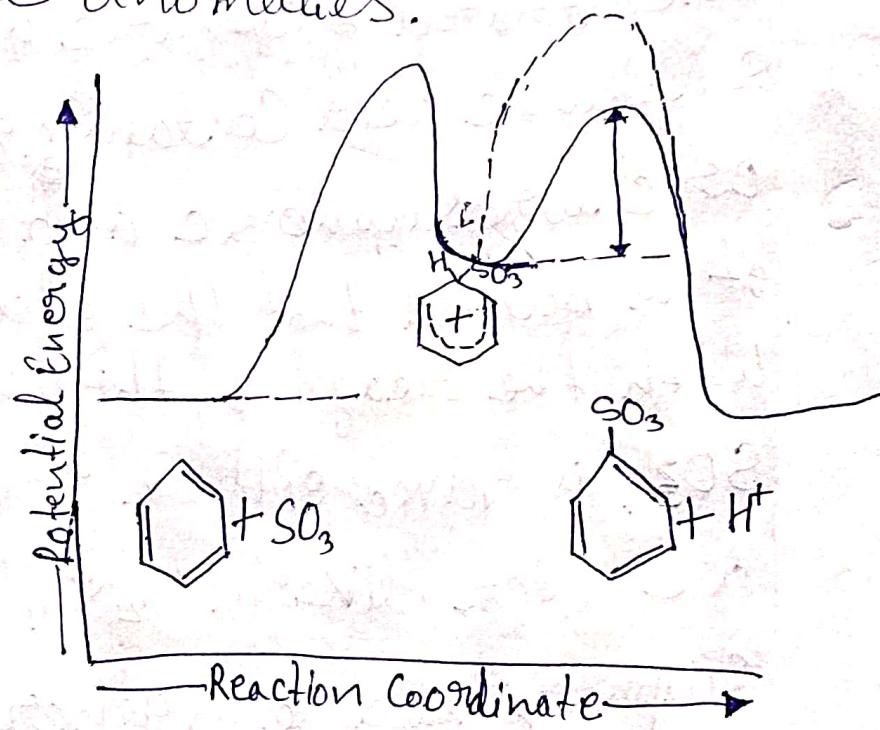
Sulphonation is another synthetically important reaction. It is often accomplished with Concentrated sulphuric acid or fuming Sulphuric acid containing excess of  $\text{SO}_3$  or chlorosulphonic acid  $\text{ClSO}_2\text{OH}$ .

It is believed that the electrophile varies with the reagent, though in all cases  $\text{SO}_3$  is involved either free or along with a carrier, like in  $\text{H}_2\text{SO}_4(\text{SO}_3 + \text{H}_3\text{O}^+)$  or  $\text{HSO}_3\text{O}_7$ . Sulphur trioxide is generated from sulphuric acid as follows  $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{H}_3\text{O}^+ + \text{SO}_3$

The mechanism of sulphonation of benzene is given below:



Sulphonation is different from other aromatic electrophilic substitution reactions. Firstly, it is reversible and secondly, it shows some amount of isotopic effect which is totally absent in other cases. Let us have a look at the potential energy diagram (Fig.) of sulphonation reaction to understand these anomalies.



We see that once the  $\sigma$ -complexed benzenium intermediate is formed; the energy barriers on either side of the intermediate are roughly of the same magnitude. This means that the intermediate can cross over to the product and can also come back to the reactant. This accounts for a reversible nature. Now, if we

have the deuterated substrate, then the potential energy diagram gets slightly modified (dotted curve). The barrier to Step II becomes higher as it now involves the cleavage of C-D bond. The barrier for Step I, on the other hand, remains the same as it pertains to  $\sigma$ -Complex formation. The rate of its reverting back to reactants is higher than its conversion to the product. Therefore, there is a net decrease in the overall rate of ~~Step II~~ Sulfonation for deuterated substrate - It shows a kinetic isotope effect. The loss of proton (Step II) is the slowest step (0.6s). The equilibrium in step III lies to the left as aryl sulphonic acids are strong acids.

In the case of other electrophilic substitutions, in contrast, energy barrier for the first step is much higher than that for the second step even for a deuterated substrate.