

15.17 Energy Diagram for Electrophilic Aromatic Substitution Reactions

Like any other reaction, the rate of electrophilic substitution depends on the difference between energy of transition state and ground state of the reactants, *i.e.*, energy of activation, E_{act} . Energy diagram for a typical electrophilic aromatic substitution can be constructed as in Fig. 15.1 (note that in the energy diagram, formation of π -complex is ignored because in most of reactions the rate determining step generally involves the formation of σ -complex).

Note that the energy of activation for the formation of σ -complex from benzene and the electrophile is much larger than the energy of activation for the formation of substituted benzene from σ -complex. This is because the formation of σ -complex is highly endothermic since in this change benzene ring loses its resonance energy to form non-aromatic compound. On the other hand, decomposition of a σ -complex to give the substituted benzene is highly exothermic because in this change the benzene ring regains its resonance energy, *i.e.*, non-aromatic σ -complex is changed to aromatic compound (substituted benzene).

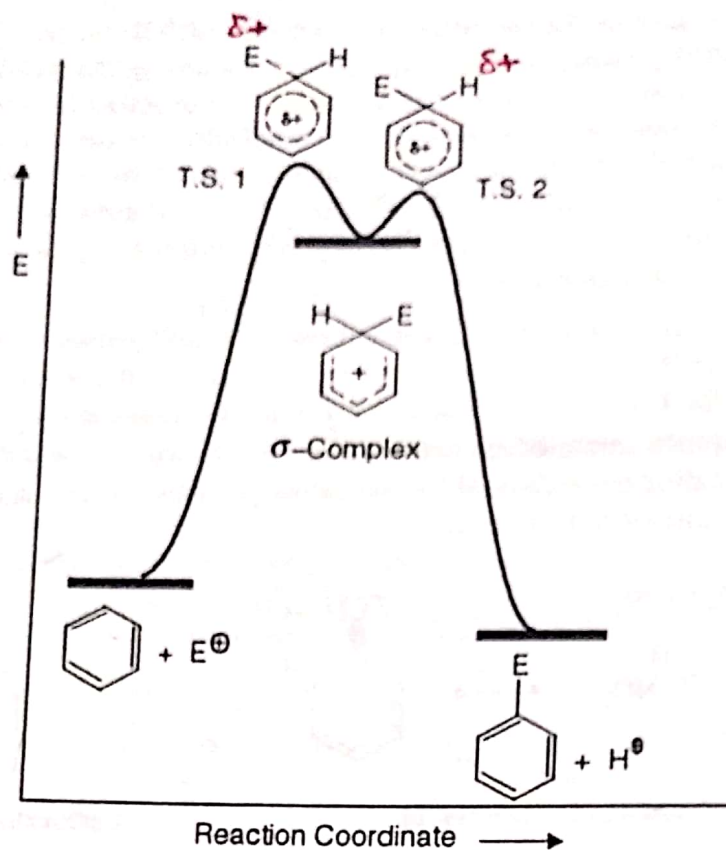
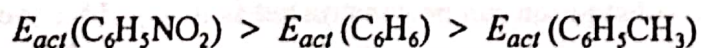


Fig. 15.1 Free-energy diagram for typical aromatic electrophilic substitution ignoring π -complex σ -complex lies in the valley between the two transition states (T.S) 1 and 2. In the transition state 1, the electrophile (E^+) has yet only partially attached to the benzene ring, while in the transition state 2, the bond between carbon atom and proton is only partially broken.

Similar energy diagrams can be constructed for substituted aromatic rings and the rate of substitution of the two compounds and also the rate of substitution at *o*-, *p*- or *m*- positions can be ascertained by measuring the height of the energy barrier between the reactant and the transition state. The lower the value of the height, *i.e.*, lower the value of energy barrier for a particular σ -complex, lower is the activation energy and more favourable is its formation. This will become clear by studying following examples.

Comparison of energy of activation (energy diagrams) of benzene, toluene and nitrobenzene. Fig. 15.2 reveals the following relative order of energy of activation for the electrophilic substitution of the three compounds.



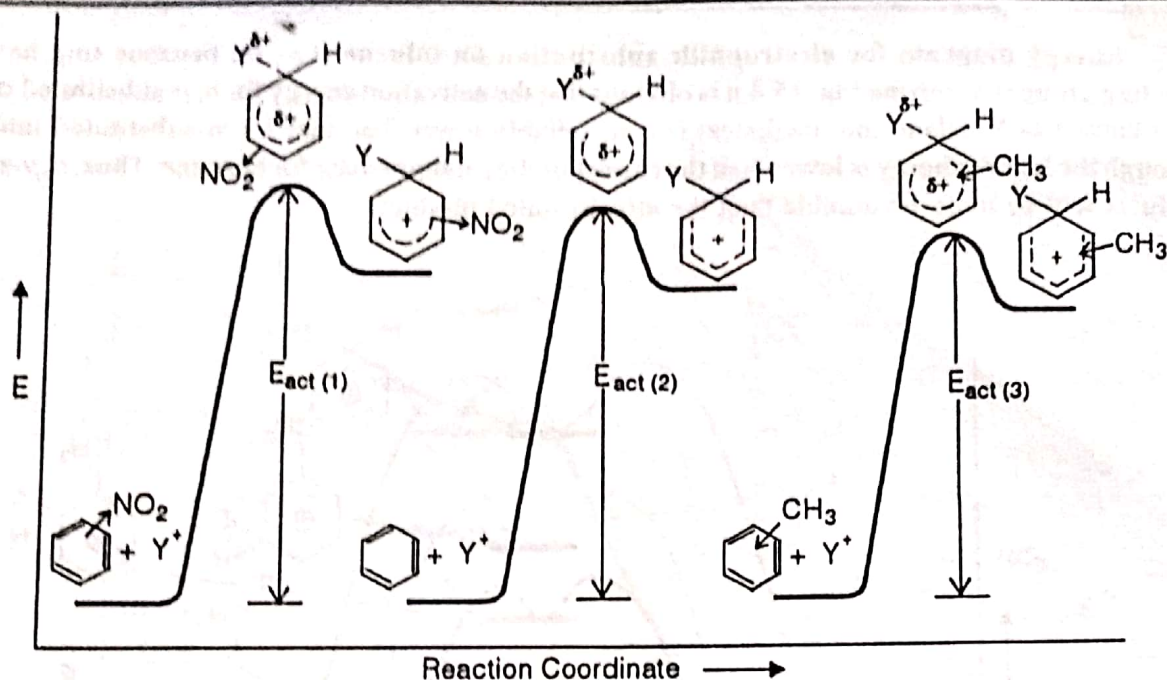


Fig. 15.2 Energy diagrams for electrophilic substitution in benzene, nitrobenzene and toluene.

Where $E_{act(1)}$ = Energy of activation for an electrophilic attack on nitrobenzene.

$E_{act(2)}$ = Energy of activation for an electrophilic attack on benzene

$E_{act(3)}$ = Energy of activation for an electrophilic attack on toluene.

Note that the initial potential energy for the three compounds is shown equal only because of convenience for comparison.

Thus, toluene having minimum energy of activation will undergo electrophilic substitution most readily, while nitrobenzene with most difficulty.

Note that the E_{act} is substantially greater than E_{act} , because of the combined effect of resonance and inductive effects of the $-NO_2$ group in nitrobenzene. Actually, the potential energy of nitrobenzene is lower than that of benzene due to resonance (See Fig. 15.3, also Fig. 15.5). Similarly, potential energy of σ -complex obtained from nitrobenzene is higher than that of σ -complex obtained from benzene an account of inductive effect of the nitro group (Fig. 15.3).

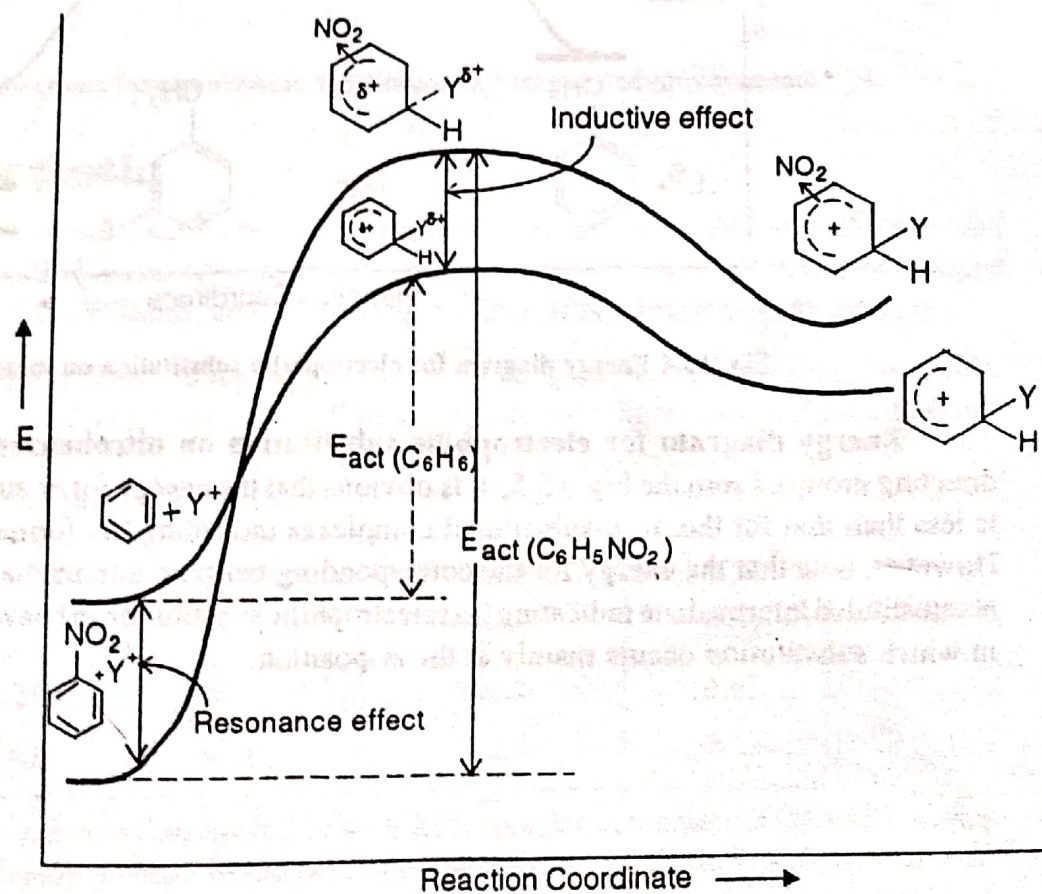


Fig. 15.3 Energy diagram for electrophilic substitution on C_6H_6 and $C_6H_5NO_2$ illustrating higher value of E_{act} for nitrobenzene than that of benzene.