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[II] Electron Tunnelling

In electron transfer processes, the electron migrates from one energy surface, representing the dependence of the energy of DA on its geometry to another energy surface, representing the energy of D^+A^-. We can express the potential energy surfaces of the two complexes (the reactant complex DA and the product complex D^+A^-) by parabolas, characteristic of simple harmonic oscillators with the displacement coordinate which correspond to changing geometries [Fig. (31)]. This coordinate shows a collective mode of donor, acceptor and solvent. According to Franck-Condon principle, the nuclei do not have the time to move when the system passes from the reactant to product surface due to electron transfer so that electron transfer can take place only after thermal fluctuations and bring the geometry of DA to q^* [Fig. (31)], the value of nuclear coordinate at which the two parabolas intersect.

The factor $\kappa\nu$ is a measure of the probability that the system will change from reactants DA to products D^+A^- at q^* by electron transfer within the thermally excited DA complex. For understanding this process, we consider the effect that the rearrangement of nuclear coordinates has electronic energy levels of DA and D^+A^- for a given distance r between D and A. [Fig. (32)]. In the beginning, the electron to be transferred occupies the HOMO (highest occupied molecular orbital) of D and the overall energy of DA is lower than that of D^+A^- [Fig. (32a)]. During the rearrangement of nuclei to a configuration shown by q^* in figure (31), the highest occupied electronic level of DA and the lowest unoccupied electronic level of D^+A^- become, degenerate and electron transfer becomes energetically feasible [Fig. (32b)]. Over a short distance, r, the mechanism of electron transfer is tunnelling through the potential energy barrier shown in figure (31). The height of the barrier increases with the ionisation energies of DA and D^+A^- complexes. When an electron moves from HOMO of D to LUMO of A, the system relaxes to the configuration expressed by q_0^P [Fig. (32)]. From
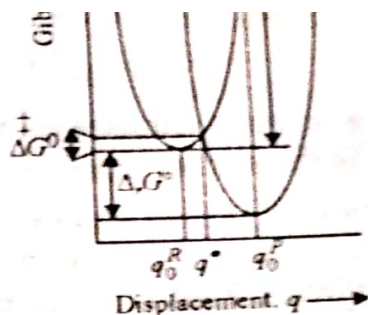

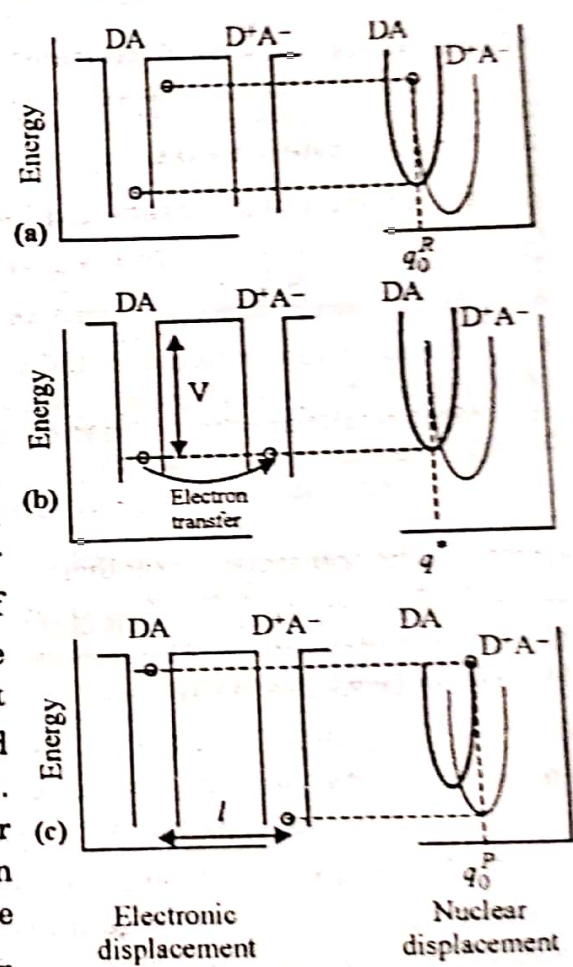Fig. 31. The Gibbs energy surfaces of the complexes DA and D^+A^- involved in

Fig. 32. Mechanism of electron tunnelling in electron transfer

figure 32(c), it is clear that the energy of D^+A^- is lower than that of A, showing the thermodynamic tendency of A to remain reduced and for D to remain oxidised.

The rate of electron tunnelling from an energy level mentioned by the wavefunction Ψ_D to a level mentioned by the wavefunction Ψ_A is proportional to the matrix element $<\Psi_A|\hat{H}_{DA}|\Psi_D>$, where $\hat{H}_{DA}$ is Hamiltonian that mentions the coupling of the electronic wavefunction. When the coupling is weak, then

$$|<\Psi_A|\hat{H}_{DA}|\Psi_D>|^2 = |<\Psi_A|\hat{H}^0_{DA}|\Psi_D>|^2\, e^{-\alpha r} \qquad \ldots (2)$$

where r is edge to edge distance between D and A, α is a parameter that gives the sensitivity of the coupling matrix element to distance and $<\Psi_A|\Psi^0_{DA}|\Psi_D>$ is the value of electronic coupling matrix element when $r = 0$, i.e., when D and A are in contact. The dependence of exponential on distance in equation (2) is the same as the exponential decrease in transmission probability through a potential energy barrier that we generally encounter in tunnelling through barriers.

The rate constant for electron transfer, k_{et} is given by the following equation

$$k_{et} = \frac{2|<\Psi_A|\hat{H}_{DA}|\Psi_D>|^2}{h}\left(\frac{\pi^3}{4\pi RT}\right)^{1/2} \exp\left(-\Delta G^0/RT\right)$$

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