COMPARISON OF THE TUNNELING PROBABILITIES FOR DIFFERENT CLASSES OF PROTON TRANSFER REACTIONS

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Previously we had explained the decrease in the preexponential factor with increasing hydrogen adsorption energy on metals by stating that the proton under these conditions is more strongly localized, and hence has a lower probability for its passage underneath the barrier. From this point of view one could expect very low tunneling probabilities for homogeneous proton transfer reactions, where the energy of the bonds being formed is about three to four times that of the M–H bond energy. It is known, on the other hand, that extremely high rates prevail for a wide selection of such reactions (the reactions of O–H or N–H acids), so that the tunneling probability must be close to one. Homogeneous reactions of C–H acids, on the other hand, are characterized by strongly reduced rates.

It seems possible to us to explain all these observations from a unified point of view by taking into account that the wave-function overlap of the initial and final state is highly dependent, not only on the degree of localization of the proton but also on the distance over which it is transferred. In homogeneous proton transfer from O–H acids, the donor and acceptor are linked by a hydrogen bond. The length of an O–H...O hydrogen bond is about 2.7 Å, the length of a covalent O–H bond is almost 1.0 Å. Thus, the proton is transferred over a distance $\Delta r \simeq 0.7$ Å. Where hydrogen bonds are not formed or are very weak, the proton transfer distance can be estimated from the sum of the van der Waals radii of the acceptor atom (R_A) and of hydrogen (R_H), which govern the approach of the molecules preceding proton transfer, and from the sum of their covalent radii (r_A and r_H):

$$\Delta r = R_A + R_H - r_A - r_H.$$

For a number of atoms one has $R - r \simeq 0.8$ Å, on an average, so that $\Delta r \simeq 1.6$ Å. The formation of strong hydrogen bonds is unlikely, both during electrode reactions (low electronegativity of the metals) and in the reactions of C–H acids (low polarity of the C–H bond). Hence for such processes the proton transfer distances are much longer than for the reactions of O–H and N–H acids, and thus the tunneling probability and the corresponding reaction rate are lower.

The above values for Δr refer to changes in the equilibrium distances, and hence can only serve as a relative characteristic of the different processes. The absolute values of Δr during the elementary act itself probably are smaller, since an approach of the molecules must be profitable, inasmuch as by the expenditure of additional activation energy one attains a large gain in the tunneling probability.

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