

Stepwise and Concerted Reaction Paths Triggered by Electrochemical, Homogeneous, and Photoinduced Electron Transfer

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Electron transfers to or from molecules are very often accompanied by a profound intramolecular reorganization that may be as dramatic as the cleavage of a bond. These strong structural changes may occur concertedly or successively to electron transfer. In the first case, the model developed for dissociative electron transfer has been illustrated by many experimental examples of heterogeneous (electrochemical) and homogeneous thermal reactions. It has long been considered on intuitive grounds that photoinduced dissociative electron transfers are typified by a unity quantum yield, this rule serving as diagnostic criterion for differentiating concerted from stepwise processes. In fact, the quantum yields of photoinduced dissociative electron transfers may well be less than unity on account of partitioning between back electron transfer and product formation at the intersection of the potential energy surfaces of the product and ground state reactant systems. The photoinduced reductive cleavage of CCl_4 provides an example of this behavior. The competition between the concerted and stepwise pathways is primarily depending upon molecular structure factors, namely the bond dissociation energy, the energy of the orbital hosting the electron (or the hole) transitorily and of the oxidation potential of the leaving group, as illustrated by a set of experimental examples. In borderline situations, the passage from one mechanism to the other may be triggered by a variation of the incoming electron energy. Several electrochemical and homogeneous examples of this change of mechanism have been found. It is also interesting to compare, within the same conceptual framework, electrochemically and photochemically induced reactions to the same substrate to evaluate the interplay of intramolecular and external factors in this respect.