Concepts and Tools for Mechanism and Selectivity Analysis in Synthetic Organic Electrochemistry

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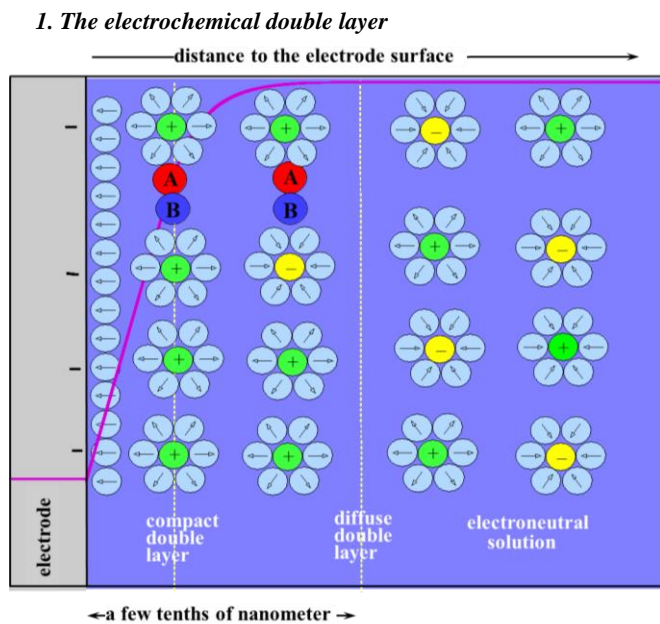## 1. The electrochemical double layer

Fig. S1. Electrical double layer at the interface between an electronic conductor serving as electrode and a solution containing solvated cations and anions (the solvent is represented by an electrical dipole). The magenta line stands for the electrical potential profile between the electrode and the bulk of the solution. The red and blue circles represent the reactant A and the product B in case of an elementary electrochemical reaction. They are usually assumed to stand in the middle of the compact double layer when electron transfer from (or to) the electrode takes place. The figure represents a case where the electrode is negative to the point of zero charge. It has to be symmetrically inverted if the electrode is positive to the point of zero charge.

2. The electrochemical reduction of vicinal dihalides into the corresponding olefins (S1)

This reaction has been the object of particularly detailed studies involving several families of catalysts (figure S2). Among them, electro-generated anion radicals follow the redox catalysis mode as defined earlier. The ensuing activation-driving force relationship – strictly speaking a parabola – is close to a $1/0.12$ V^{-1} slope –straight line. The TOF_{max} value at zero-driving force essentially reflects the intrinsic electron transfer properties of the substrate since the reorganization energy of the (largely delocalized) anion radicals is small. The two other families (open circles – dotted line and solid square -dashed-dotted line) stand much over the outersphere line. They are typical illustrations of chemical catalysis as defined earlier. The representation of the data by means of catalytic Tafel plots dramatically underscores the superiority of the chemical catalysts over the redox catalysts. This is also the case as concerns stereospecificity as revealed by detailed studies of a series of other vicinal dihalides (S1).
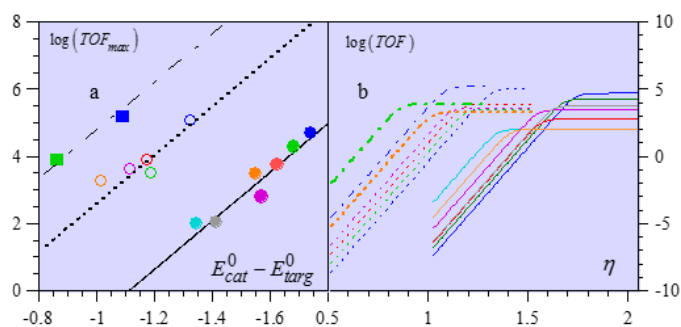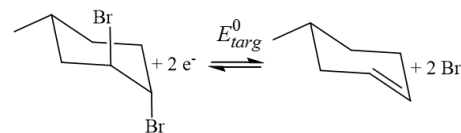

Fig.S2. Catalysis of the electrochemical reaction of the upper scheme by anion radicals of aromatic hydrocarbons and of H$_2$TPP, ZnTPP, CuTPP (solid circles and solid lines), Fe$^{II/I}$ porphyrins (open circles and dotted lines), Co$^{II/I}$ porphyrins (solid squares and dashed-dotted lines), from the data in ref. (22), potentials in V, TOF in s^{-1}). a: variation of the maximal TOF with the catalyst standard potential. b: catalytic Tafel plots.

References

S1. Lexa D, et al. (1990) Outer-sphere and inner-sphere processes in reductive elimination. Direct and indirect electrochemical reduction of vicinal dibromoalkanes. J. Am. Chem. Soc. 112(17):6162-6177.