

Stepwise and Concerted Electron Transfer/ Bond Breaking Reactions. Similarities and Contrasts in Thermal and Photoinduced processes.

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Abstract. The electrochemical (cyclic voltammetry) and photoinduced (fluorescence quenching, quantum yields) reductive cleavages of four compounds (figure 1), 4-cyano- α -trifluorotoluene (**1**), 4-cyanobenzylmethylphenyl sulfonium (**2**) and 4-cyanobenzyl chloride (**3**) will be compared in terms of concerted vs. stepwise mechanisms.

Bearing in mind that an increase of the thermodynamic driving force shifts the mechanism from concerted to stepwise and that the driving force is larger under photochemical than under electrochemical conditions, it will be shown that **1** is a typical example where a stepwise mechanism is followed with compatible kinetic characteristics under both regimes. **3** undergoes a concerted electrochemical reductive cleavage and the same mechanism is followed in the photoinduced reaction with consistent kinetic characteristics. The case of **2** is of particular interest since the trend of passing from a concerted to a stepwise mechanism when going from the electrochemical to the photochemical conditions indeed results from the analysis of the experimental results. The change of mechanism is however not complete since, in the photoinduced reaction, there is a balanced competition between the two pathways. Theoretical interpretation of the data will be given.

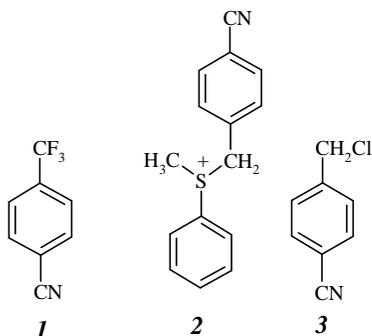


Fig.1