MUTUAL INTERACTION OF TWO REDOX ACTIVE CENTRES IN A SINGLE MOLECULE AN ELECTROCHEMICAL APPROACH

Jiri Ludvik[1]

[1] J. Heyrovsky Institute of Physical Chemistry, Academy of
Sciences of the Czech Republic,
Dolejskova 3
Prague 8, CZ 182 23
Czech Republic

Mutual electronic interaction of two (or more) redox active groupings within one molecule is an important phenomenon characterizing extent of electron delocalisation between the concerned groups. Electrochemistry is one of the most useful experimental approaches to such investigations. Molecules with two redox active centers represent fundamental units for organized nanostructures and supramolecular devices.

The interaction can be of various extents depending on the groups themselves and on the spacer between the centers. There is a continuous passage from negligible interaction representing an electronic isolant to the full delocalisation and aromaticity (in cyclic molecules).

Several types of such “bitopic” molecules were electrochemically investigated in order to explain their often unexpected redox properties. Already in sixties, Zuman 1 studied N,N-polymethylene-bis-sydnones in aqueous buffers and started thus the research of mutual interactions of two identical redox centres connected by a saturated chain. Bis-1,1- pyridinium dications are analogous molecules with two identical reducible centres (pyridinium cation). In this case not only saturated, but also phenylene-linked molecules were investigated in aprotic solvents2. Other examples are aromatic or heteroaromatic systems of type R1-Ar-R2, where is generally medium extent of interaction which is often described by LFER (Linear Free Energy Relationship) 3. Strong interaction can be observed in the series of diazinyl-methyl-ketoximes, where the number and position of nitrogens in the heterocycle changes substantially the reducibility of the oxime grouping 4. In the case of hybrid phosphinoferrocene ligands, the interaction is so strong, that an intramolecular electron transfer is observed and the phosphine grouping is oxidised only through the Fe(III)-Fe (II) redox system 5. On the other hand, the heterocyclic 1,2,4-triazin-5- ones 6 exhibit no interaction between the two azomethine bonds and the recent extensive study of a series of linear azines confirm the hypothesis that the N-N bond has a single character preventing the electron delocalisation.

Acknowledgement - This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (project No. A4040304) and by the Grant Agency of the Czech Republic (project No. 203/02/0983)

References:

1. Zuman, P., Collect. Czech. Chem. Commun. 25 (1960) 3252-3264.

2. Volke, J., Urban, J. , Volkeova, V., Electrochim. Acta 39 (1994) 2049-2054.

3. Zuman, P., Substituent Effects in Organic Polarography, Plenum Press, New York 1967.

4. Cibulka, R., Liska, F., Ludvik, J., Collect. Czech. Chem. Commun. 65 (2000) 1630-1642.

5. Podlaha, J., Stepnicka, P., Ludvik, J., Cisarova, I., Organometallics 15 (1996) 543-550.

6. Ludvik, J., Riedl, F., Liska, F. and Zuman, P., J. Electroanal. Chem. 457 (1998) 177-190.