ELECTROCHEMICAL INVESTIGATION OF ELECTRON-TRANSFER PHENOMENA IN THE SERIES OF PHENOTHIAZINE AND OF RELATED COMPOUNDS II. Reductive electrocatalysis of the –CH=N- and formyl group on the phenothiazine ring

M. Jitaru, G.Petrică, L. I. Găină, and Ioan Al. Silberg

"Babes-Bolyai" University, Cluj-Napoca
Faculty of Chemistry and Chemical Engineering
11 Arany Janos str., 3400 Cluj-Napoca, Romania

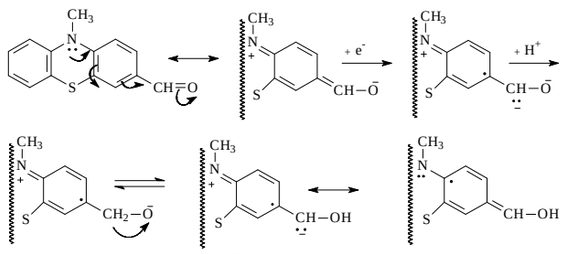
The redox properties of the phenothiazine heterocycle were thoroughly studied and its donor capacity was proved by chemical and electrochemical means [1,2]. However, much remains to be done in order to establish the influence exerted by functional groups on the redox behaviour of phenothiazine nucleus. Our investigations aimed at comparing the electronic transfer processes in the case of formyl, and of -CH=N- groups.

In our earlier papers concerning the electrochemical behaviour of some oligophenothiazines in aprotic media [3] the same reversible monoelectronic process of the formation of the cationic radical has been reported. The electrochemical answer of the reducible groups on the phenothiazine nucleus in hydroalcoholic medium [4] and the donating properties of the phenothiazine nucleus [5] have been investigated.

The aldehydes and Schiff bases with phenothiazine nucleus are investigated here for the first time by electrochemical means.

Thus, as it can be seen from figure 1, the formyl group reduction process appears, for both compounds, at the same negative potential ε_0 = -1.6 V (Ag/Ag^+ reference). The delocalisation of the unpaired electron in the reduced intermediate of benzaldehyde, generates a weak stability due to mesomere structures with electronically and sterically unprotected radicalic forms, which are able to accept immediately the second electron transfer from the cathode. In the case of compound IV, the reduced intermediate (scheme 1) is characterised by a higher stability, due to the neighbouring electronic and steric effects of the heteroatoms and to its decreased adsorption capacity on the cathode; thus, the second reduction stage appeared shifted towards higher potentials, as compared to benzaldehyde. Two similar reduction stages are also present in the case of the registered cyclic voltammograme of *p-N*, *N*-dimethylamino-benzaldehyde, stressing the analogies between the pertinent substructures.

In spite of the fact that, due to the irreversibility of the processes, we were not able to determine directly the number of electrons transferred in each stage of the cyclic voltammogram, we can assume according to the value of the current (twice that of the monoelectronic transfer – fig.1, that for the reduction of the oxo group in benzaldehyde structure, two electrons are transferred in one step, whereas there are two different monoelectron reduction processes in the case of 10-methyl-3-formyl-phenothiazine – Fig. 1. The first oxidation process, situated at ~ 850 mV (figure 1) is a quasireversible monoelectronic transfer process.



Scheme 1.

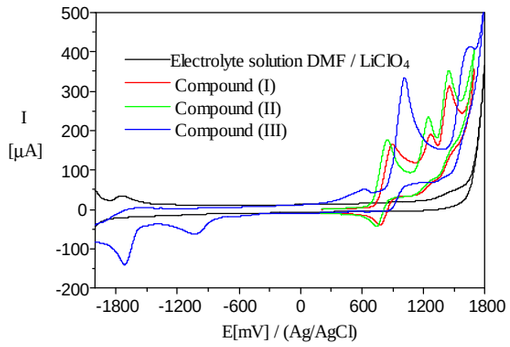


Figure 1. Cyclic voltammograms of (I), (II) and (III), 10^{-2}molL^{-1}in DMF, WE: glassy carbon RE: Ag/Ag^+ (I): 10-methyl-phenothiazine; (II):10-ethyl-phenothiazine (III): 10-methyl-3-formyl-phenothiazine

Equation A and B

$E_{ox}-E_{1/2ox}=2.203\ R\ T\ n^{-1}\ F^{-1}=0.060\ n^{-1}$ (A)

$I_p=2.72\ 10^5\ n^{3/2}\ D^{1/2}\ A\ v^{1/2}\ c_o$ (B)

leads to a calculated number of exchanged electrons (n=0.66), but a better approximation was obtained by using the eq. B, which gave n=1.01. Thus, each of the two approximations led to a monoelectronic transfer process.

Our investigations illustrated, by means of cyclic voltammetry, the influence of the electronic effects of some substitutes upon the electrochemical behaviour of the phenothiazine nucleus.

Thus, N-alkyl substitution does not modify the characteristic phenothiazine pattern with a monoelectronic quasireversible oxidation process (E_{ox}=850 mV), followed by two supplementary irreversible oxidation steps (E_{ox1}=1250 mV, E_{ox2}=1440 mV). On the contrary, the formyl group, as a substitute of the phenothiazine nucleus, alters the reversibility of the phenothiazine first monoelectronic oxidation process, probably due to the low stability of the intermediate radical cation (Scheme2) affected by the electron withdrawing mesomere effect, and, in the same time, shifts this oxidation potential towards greater values (E_{ox}=1015 mV). Rather surprisingly, the -CH=N- group, from the Schiff base structure, does not alter the reversibility of the oxidation process characteristic to the phenothiazine moiety, even though, by its mesomere effect, shifts, as expected, the oxidation potential towards greater values (E_{ox}=1107 mV).

REFERENCES

1. B. Paduszek and M.K. Kalinovski, *Electrochimica Acta*, **1983**, 28(5),639.
2. N. Sulcova, I. Nemec, K. Waisser, H. L. Kies, Microchem. J., **1980**, 25, 55.
3. M. Jitaru C. Cristea and Ioan A. Silberg, *Rev. Roum. Chim.*, **1999**, 44(9), 863.
4. C. Cristea, C. Filip, I. Silaghi-Dumitrescu, I. A. Silberg, *Rev.Roum.Chim.***2000**,45(7-8), 639.
5. M. Jitaru, J. Stroka, Z. Galus, C. Cristea et I.A. Silberg , *Journée d'électrochimie*, **1997** Montreal, Canada, CA 8-14.