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ELECTROCHEMICAL OXIDATION  
OF VARIOUS ORGANIC  $\Pi$ -ELECTRON SYSTEMS

The comparative studies of the series of organic  $\Pi$ -electron system have been carried out using the cyclic voltammetry. The aim of this work was to generate free radicals from some organic compounds under study, and then to detect them with using the cyclo-voltammetric methods. Therefore the following compounds have been oxidized: anthracene, triptycene, p-terphenyl, 1,8-dihydroxy-9-anthrone, 9-anthrone, azobenzene, 4,4'-dimethylazobenzene, 4,4'-di-tert-butylazobenzene, 2,5-dimethyl-1,3,4-thiadiazole, 2,5-di-tert-butyl-1,3,4-thiadiazole, and N,N,N',N'-tetramethyl-p-phenylenediamine. I have been encouraged to carry out this work, since only a few occasional works using ESR have so far been performed for some of these compounds [1, 2]. This novel ESR study has confirmed that anthracene, triptycene, p-terphenyl and azobenzene are apt to form free radicals in their solutions in dichloromethane. Additionally, only the voltammetric results could enable to arrange the studied compounds in some order fairly parallel to their oxidation potentials, which reflect their ability to be oxidized to free radicals.

Several values of the oxidation potentials for anthracene in various solvents have been reported. For example, S w a n h o l m [3] has found that its oxidation potential ( $E_{ox}$ ) is equal to 1.31 V (vs SCE) in  $CH_2Cl_2$ , whereas H a m m e r i c h [4] has reported value of  $E_{ox} = 1.40$  V (vs SCE) in  $CH_2Cl_2$ .

Only an occasional work has been done on the electrooxidation of azo compounds. F l o r e n c e [5] has reported that azobenzene dissolved in 5% aq. methanol is not oxidized over the potential range of the pyrolytic graphite electrode (1.2 V vs SCE), and the strongly

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electron-releasing groups, such as  $N(CH_3)_2$  and OH, must be present to obtain in such system an oxidation wave as well as that such compounds undergo a 2-electron oxidation. This result is in agreement with other works [6]. There are no available literature data about oxidation of terphenyl. Parker et al. [7] have compared the properties of several p,p'-dimethoxypolyphenyls, with including p,p'-dimethoxyterphenyl, using the voltammetric method. He found the first charge transfer for those compounds to be a quasi-reversible one-electron with the peak separation being slightly greater than 60 mV. Also the second oxidation step, from a cation radical to a dication, was reversible for all the compounds. Parker found the following oxidation potentials for p,p'-dimethoxyterphenyl measured in the mixture composed of  $CH_2Cl_2$  - TFA - TFA(45 : 5 : 1) Ep,  $a_{n_1} = 1,65$  V (vs SCE). Hand et al. [8] have explained the marked stability of cation radicals formed from N,N,N',N'-tetramethyl-p-phenylenediamine in acetonitrile as the result of the strong delocalizing power of the second dimethylamino group. Zweg [9] has reported the polarographic half-wave oxidation potential of the aforementioned p-phenylenediamine in acetonitrile, at a rotating platinum electrode, to be equal to

$$E_{1/2} = -0.10 \text{ V vs Ag/0.01 M Ag}^+$$

Although it is well recognized that the pharmacological activity of most natural or synthetic anthraquinones involves the corresponding anthrones, their way of action is not yet understood. Among these compounds, anthralin (1,8-dihydroxy-9-anthrone) is of particular interest [10], as it is one of the chief drugs in the up-to-date treatment of psoriasis and related skin diseases.

#### EXPERIMENTAL

The cell used for the voltammetry was a two-compartment vessel with working and counter electrodes in one chamber, and separated from chamber of the reference electrode by a sintered glass.

Platinum gauze electrode was used as the working electrode in all measurements.  $\text{Ag}/\text{Ag}^+$  saturated electrode was used as the reference electrode in the  $\text{CH}_2\text{Cl}_2$  - TFA - TFAn (23 : 1 : 1) mixture and 0.1 M  $\text{Bu}_4\text{NBF}_4$  as a supporting electrolyte. This mixture was chosen as the best one to maintain optimum conditions for recording the well-resolved voltammograms. The symbols used above indicate, respectively:

TFA - trifluoroacetic acid,

TFAn - trifluoroacetic anhydride.

Only for N,N,N',N'-tetramethyl-p-phenylenediamine, azobenzene and 9-anthrone the voltammograms were recorded in acetonitrile.  $\text{Ag}/0.1 \text{ M Ag}^+$  was used here as the reference electrode, and 0.1 M  $\text{LiClO}_4$  as a supporting electrolyte. All the measurements were carried out using a PG-30-1 A potentiostat (with IRe compensation) with a linear sweep generator [11]. Also all voltammograms of the studied compounds were recorded with the a voltage sweep rate equal to 100, 200, 300, 400, 500 and 600  $\text{mV s}^{-1}$  at  $298 \pm 0.2 \text{ K}$ .

Dichloromethane was stored over  $\text{P}_2\text{O}_5$  for few hours, and, then it was redistilled twice, 4,4'-di-tert-butylazobenzene, 4,4'-dimethylazobenzene, 2,5-dimethyl-1,3,4-thiadiazole and 2,5-di-tert-butyl-1,3,4-thiadiazole were synthesized by the known methods [12]. Other compounds listed below were commercially available, and they were used without any further purification.

## RESULTS AND DISCUSSION

The following values of the anodic half-peak potentials ( $E_p$ , a/2) have been found for the studied  $\pi$ -electron systems in the mixture made of  $\text{CH}_2\text{Cl}_2$  - TFA - TFAn (23 : 1 : 1) on the platinum electrode (sweep rate, 200  $\text{mV/s}$ );  $\text{Ag}/\text{Ag}^+$  was used as a reference electrode.

Table 1

	Ep, a/2
anthracene	0.67
tritycene	1.35
p-terphenyl	1.10
azobenzene	1.28
4,4'-dimethylazobenzene	1.40
4,4'-di-tert-butylazobenzene	1.41
1,8-dihydroxy-9-anthrone	1.33
2,5-di-tert-butyl-1,3,4-thiadiazole	1.65
2,5-dimethyl-1,3,4-thiadiazole	1.69

c = 1.0 mM.

The following values of the anodic half-peak potentials (Ep, a/2) have been found in acetonitrile for the studied compounds vs Ag/0.1 M Ag<sup>+</sup>. Sweep rate 200 mV/s.

Table 2

	Ep, a/2
N,N,N',N'-tetramethyl-p-phenylenediamine	-0.28
9-anthrone	1.91
azobenzene	1.38

c = 1.0 mM.

Only for anthracene in the CH<sub>2</sub>Cl<sub>2</sub> - TFA - TFA<sub>n</sub> (23 : 1 : 1) mixture containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M), and for N,N,N',N'-tetramethyl-p-phenylenediamine in CH<sub>3</sub>CN containing LiClO<sub>4</sub> (0.1 M), the reversible one-electron oxidation peak were observed. Voltammograms for all other compounds do exhibit the irreversible or, as for azobenzene, the quasi-reversible oxidation peaks. On the

reverse scan, merely for anthracene, N,N',N'-tetramethyl-p-phenylenediamine, p-terphenyl and the azobenzene, the reduction peaks were observed. There was no temperature effect on a shape of the voltammograms under study as well (drastic decrease in temperature had not improved their shape). Full explanation of these effects requires further studies. The anodic oxidation of anthracene has extensively been studied by other authors [13-15], and it has been used as a model compound in order to establish the one-electron oxidation pathway of aromatic hydrocarbons in aprotic media.

Similarly, in our work we have used anthracene as the model compound. The value of the anodic peak potential measured by us in the  $\text{CH}_2\text{Cl}_2$  : TFA : TFA $\cdot$ n (23 : 1 : 1) mixture in reference to the silver chloride electrode is equal  $E_{p, a/2} = 1.15$  V. This potential is close to values reported by S w a n h o l m [2]. The value of the anodic half-peak potential  $E_{p, a/2} = 0.67$  V listed in Tab. 1 was measured in reference to the silver electrode (Ag/Ag $^+$  saturated).  $E_{p, a/2}$  is much lower for anthracene than for triptycene and p-terphenyl. It indicates that it is much easier to form a free cation radical from anthracene than from other two hydrocarbons.

Similarly as P a r k e r [17] for p,p'-dimethoxyterphenyl I have observed also the two-step oxidation of terphenyl the shape of waves corresponding to these two steps differ considerably for each of them. Only for the first of them the cation reduction peak was observed. But the quotient of the cathodic and the anodic peak currents was lower than unity ( $i_c/i_a$ ). It indicates that the electrochemical oxidation is followed here by a chemical reaction. The half-peak potential found for triptycene equals to 1.35 V (vs Ag/Ag $^+$  saturated).

It was quite interesting to compare the ability to be oxidized to the cation radicals of discussed above three hydrocarbons with 9-anthrone and 1,8-dihydroxy-9-anthrone. The fact that anthralin and anthrone are able to form free radicals was confirmed by earlier studies [10].

I have found for 1,8-dihydroxy-9-anthrone  $E_{p, a/2} = 1.33$  V (vs Ag/Ag $^+$  saturated). The half-peak potential for anthrone was so high (it was close to the decomposition potential of the mixed

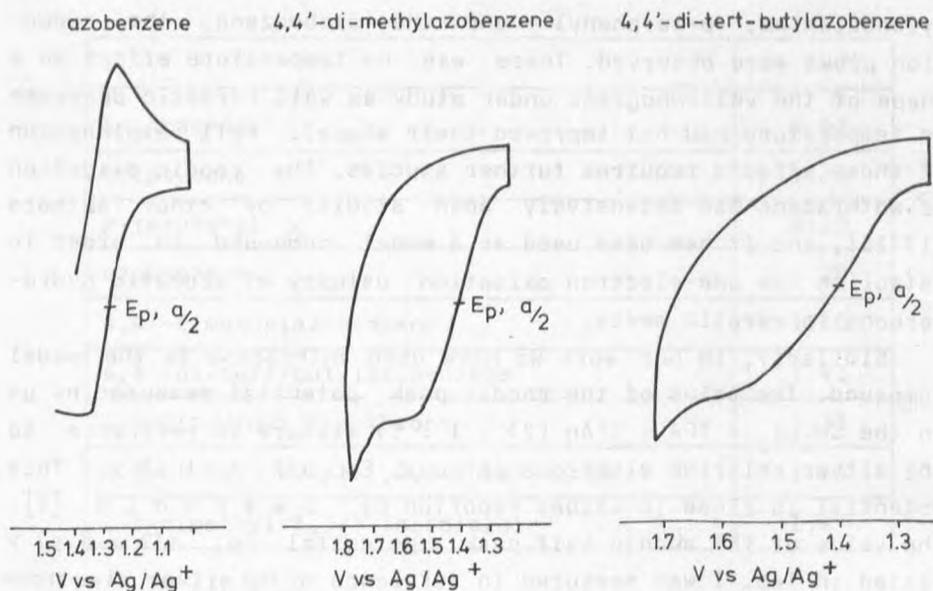


Fig. 1

solvent  $\text{CH}_2\text{Cl}_2$  : TFA : TFAn) that it was necessary to repeat the measurements in acetonitrile containing  $\text{LiClO}_4$  (0.1 M).  $E_{p, a/2}$  was found to be equal to 1.91 V (vs  $\text{Ag}/0.1 \text{ M Ag}^+$ ). New results would indicate that interaction between the C-H bond in position 10 for 1,8-dihydroxy-9-anthrone is much weaker than for 9-anthrone.

It is also known that the increase in the activity against psoriasis for different anthrons is arranged according the following order: 9-anthrone, 1-hydroxy-9-anthrone, 1,8-dihydroxy-9-anthrone. We have also observed considerable differences between azobenzene and its 4,4'-disubstituted derivatives. Only for azobenzene in the  $\text{CH}_2\text{Cl}_2$  : TFA : TFAn mixture the one-electron quasi-reversible oxidation peaks were observed, whereas for other two compounds under study the oxidation peaks were irreversible (see Fig. 1).

Also their oxidation potentials differ considerably.  $E_{p, a/2} = 1.28 \text{ V}$  (vs  $\text{Ag}/\text{Ag}^+$  saturated) for azobenzene. The oxidation half-peak potentials for 4,4'-dimethylazobenzene and for 4,4'-di-tert-butylazobenzene are equal to 1.40 V and 1.41 V (vs  $\text{Ag}/\text{Ag}^+$

saturated), respectively. The difference between azobenzene and its derivatives can be explained as the result of greater stability of the azobenzene cation radical than those obtained from two other compounds. Similarly, the ESR measurements carried out in the analogous to my mixture [2], in conjunction with the electrolysis, proved that it was much easier to obtain well-resolved spectrum for azobenzene than for its 4,4'-disubstituted derivatives. The anodic half-peak potential was also found for azobenzene ( $E_p, a/2 = 1.38$  V (vs Ag/0.1 M)). Azobenzene was used here as the reference substance to enable comparison of the oxidation potentials in  $\text{CH}_2\text{Cl}_2$  listed in Tab. 1 with those found in  $\text{CH}_3\text{CN}$  and collected in Tab. 2. N,N,N',N'-Tetramethyl-p-phenylenediamine has been used by other authors as the model system for biological studies requiring a reversible, one-electron redox system, most notably in the pioneering work of M i c h a e l i s [16].  $E_p, a/2$  measured by me for this compound in acetonitrile equals to  $-0.28$  V vs Ag/0.1 M  $\text{Ag}^+$ . This value is slightly lower than that reported by Z w e i g [9] who used a rotating platinum electrode.

However, also my voltammograms confirmed a marked stability of the generated cation radical and the dication obtained from this oxidation. Finally, I was concerned to compare the oxidation potentials for all the aforementioned compounds with those of 2,5-dimethyl-1,3,4-thiadiazole and 2,5-di-tertbutyl-1,3,4-thiadiazole. The value of the anodic half-peak potential for the former one is slightly higher than that for the latter. It means that alkyl groups substituted in positions 2 and 5 influence in a very limited way the oxidation potentials for the two thiadiazoles. Presumably, an electron hole in radicals of these compounds is localised on the sulfur atom. This conclusion seems to be supported by the work of F a b r e t t i [17], who studied 2,5-dimethyl-1,3,4-thiadiazole. He proved the coordination of this azole through the sulfur atom.

Listed in Tab. 1 and 2 the half-peak oxidation potentials reflect the ability of the studied compounds to form free radicals after the oxidation.  $E_p, a/2$  values increase according to the following order: N,N,N',N'-tetramethyl-p-phenylenediamine, anthracene, p-terphenyl, azobenzene, 1,8-dihydroxy-9-anthrone, trip-

tycene, 4,4'-dimethylazobenzene, 4,4'-di-tert-butylazobenzene, 2,5-di-tert-butyl-1,3,4-thiadiazole, 2,5-dimethyl-1,3,4-thiadiazole, and 9-anthrone.

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ELEKTROCHEMICZNE UTLENIANIE RÓŻNYCH ORGANICZNYCH  
 $\pi$  - ELEKTRONOWYCH UKŁADÓW

Przeprowadzono badania elektrochemicznego utleniania szeregu związków organicznych za pomocą woltamperometrii cyklicznej. Na podstawie otrzymanych wartości potencjałów utleniania w  $\text{CH}_3\text{CN}$  i  $\text{CH}_2\text{Cl}_2$  oceniono zdolność tych związków do tworzenia wolnych rodników w wyniku badanego procesu.