Polish J. Chem., **78**, 139–147 (2004)

Cyclic Voltammetry and Electronic Absorption Spectroscopy in Investigations of the Nature of the Electrochemical Reduction of Phenyldiazonium and Phenyl-*bis*-diazonium Cations

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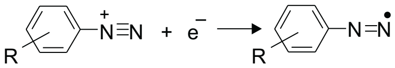
(Received November 26th, 2002; revised manuscript September 22nd, 2003)

The electrochemical reduction of phenyldiazonium and phenyl-*bis*-diazonium cations on mercury drop and platinum cathodes exhibits a multistep nature, as demonstrate the results of polarographic and cyclic voltammetry measurements. The primarily formed radicals participate in various secondary processes, as a result of which occur species absorbing UV-VIS radiation. Electronic absorption in the visible region can be ascribed to entities forming from the recombination of two azophenyl or azophenyl and phenyl radicals, originating from the one- or two-electron reduction of primarily or secondary formed cations.

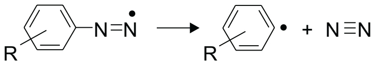
Key words: phenyldiazonium salts, electrolysis, cyclic voltammetry, electronic absorption

Arenediazonium salts have attracted attention for both cognitive and practical reasons: they are substrates in syntheses of various chemicals and drugs, are used in the production of dyes, serve as stabilizing additives and polymerization initiators, *etc.* [1–3]. These compounds readily undergo electrochemical reduction on Hg, Pt, Cu, Mg, Fe, Al and Mo electrodes [4–8], which is accompanied by electrochemiluminescence [6,7,9]. The chemical changes are believed to be initiated by the reduction [4,5,8,10],



(1)

after which elimination of molecular nitrogen may occur



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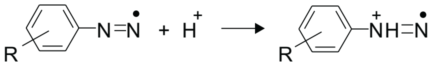
When a Hg electrode was used, diphenylmercury was formed, which demonstrates indirectly that reactions (1) and (2) occur during electrochemical reduction of the diazonium cation [5,11]. However, if reaction (1) takes place in a protic medium, another possibility exists: then radical cations,



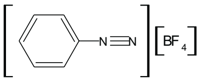
(3)

which undergo multi-step reduction to phenylhydrazines, can occur [8,12]. Electrochemical reduction of phenyldiazonium cations becomes less efficient with the passage of time, which could be due to the fact that insoluble polymeric products are deposited on the surface of the electrode [8,9].

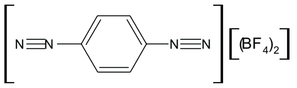
Earlier investigations provide only limited information on the products of the electrochemical reduction of diazonium salts in the liquid phase [4–7,10]. Just recently, however, we showed – using quantum chemistry methods – which products can be expected [8] and tentatively identified some of them by means of a theoretical interpretation of the spectra of the electrochemiluminescence accompanying this process [9]. In this publication we show how the reduction of phenyldiazonium and phenyl-*bis*-diazonium cations is reflected in the results of polarographic and cyclic voltammetry measurements, and what the products of this process may be following the theoretical interpretation of the electronic absorption spectra of the contents of the cathodic compartments.

EXPERIMENTAL

Materials: The objects of our investigations were phenyldiazonium **(I)** and phenyl-bis-diazonium **(II)** tetrafluoroborates



(I)



(II)

The compounds were synthesized and purified following procedures described elsewhere [13]. Their identity was confirmed by elemental analysis (performed on a GA 1108 Elemental Analyser – Carlo Erba). All solutions were obtained using doubly distilled water or p.a. acetonitrile (Aldrich). $LiClO_4$ (Aldrich) was used to prepare the background electrolyte.

Measurements: Integral and differential voltammetric curves were recorded with the use of a mercury drop electrode and a PV-1 polarograph, applying a linear sweep potential between –1.80 and +0.3 V. Cyclic voltammograms for the Pt working electrode were obtained using an Autolab instrument (Ecochemie, The Netherlands) at potentials ranging from –1.75 to +0.7 V (measured against a saturated silver/silver chloride electrode). The electronic absorption spectra of the cathodic compartment contents following electrolysis on a stationary Hg electrode were measured on an ASP Array Spectrophotometer (Sanopan, Japan). Since arenediazonium cations may be unstable, fresh solutions were always used, and all experiments were carried out at ambient temperature [10].

Deposit formation and identification: In order to analyze the deposit formed during the reduction of phenyldiazonium salts, a 0.1 M aqueous solution of **I** was electrolyzed on a large stationary mercury cathode (S = 8 cm^2) for 0.5 h at a constant current density of 1 mA/cm^2. The dark-grey deposit obtained was separated mechanically from the Hg surface, and after the removal of mercury microdroplets by means of copper wire wetted with concentrated HNO_3, the deposit was washed with methanol and dried under vacuum for 24 h at 50°C. The elemental analysis of the deposit was carried out subsequently.

Theoretical: Unconstrained geometry optimizations of molecules (Table 1) in the ground (S_0) electronic states were carried out at the semi-empirical AM1 level of theory [14], using the EF procedure [15] implemented in the MOPAC 93 program package [16]. On completion of each geometry optimization, the Hessian matrix was calculated in order to demonstrate that structures correspond to true minima [17]. The wavelengths and oscillator strength of electronic absorption transitions ($S_0 \rightarrow S_n$) were calculated using ground state geometries and the HyperChem program package [18]. In all cases, 201 ground and single excited state configurations were used owing to excitation within the HOMO–10 and LUMO+10 molecular orbitals [19]. However, to check how the size of the CI matrix influences the predicted wavelengths of $S_0 \rightarrow S_n$ transitions we also carried out calculations with 19 (HOMO–3 – LUMO+3), 51 (HOMO–5 – LUMO+5) and 99 (HOMO–3 – LUMO+3) configurations for compounds **1** and **3** (Table 1). As can be seen in Table 2, the spectral characteristics change noticeably when the number of configurations increases from 19 to 99 but only slightly upon further increase of this number to 201. We thus used 201 configurations in all calculations.

Table 1. Theoretically predicted electronic transitions in phenyldiazonium **(1)** and phenyl-*bis*-diazonium **(2)** cations and possible products of their electrochemical reduction.

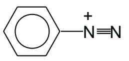
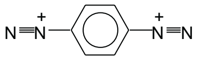
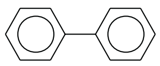
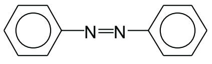
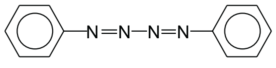
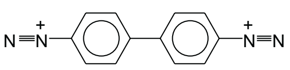
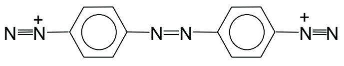
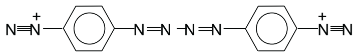
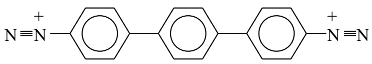
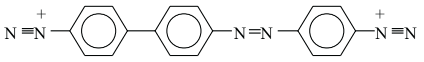
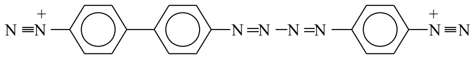
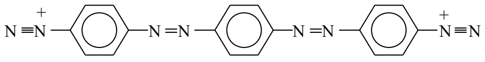
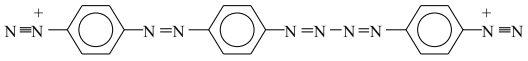
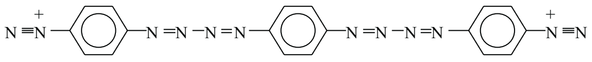
Entity		Transitions[a]
No.	Formulae	Wavelength (oscillator strength)
1		340 (0.05); 323 (0.18); 252 (0.49)
2		344 (0.10); 317 (0.14)
3		319 (0.14)
4		387 (0.03); 305 (0.12); 241 (0.42)
5		484 (0.04); 314 (0.50); 245 (~1)
6		349 (0.72); 338 (0.09); 242 (~1)
7		345 (0.62); 333 (0.07); 319 (0.17); 240 (0.67)

Table 1 (continuation)

8		342 (0.82); 328 (0.08); 293 (0.11); 233 (0.89)
9		379 (~1); 284 (0.07); 259 (0.17); 240 (0.55)
10		360 (0.93); 333 (0.33); 282 (0.08); 260 (0.11); 244 (0.14); 239 (0.22); 238 (0.35); 234 (0.05)
11		390 (0.10); 361 (~1); 310 (0.19); 289 (0.08); 263 (0.09); 242 (0.11); 241 (0.25); 232 (0.28)
12		345 (~1); 325 (0.18); 295 (0.22); 286 (0.16); 281 (0.10); 271 (0.22); 262 (0.26); 253 (0.12); 250 (0.06); 237 (0.12); 234 (0.27)
13		373 (0.07); 340 (~1); 321 (0.35); 315 (0.13); 298 (0.21); 287 (0.20); 284 (0.08); 282 (0.05); 272 (0.20); 267 (0.25); 231 (0.05)
14		382 (0.24); 325 (~1); 309 (0.14); 278 (0.09); 270 (0.22); 246 (0.11)

[a] All data correspond to the thermodynamically most stable conformers. Wavelengths are given in nm.

Table 2. Electronic transitions for various sizes of the CI matrix[a].

Compound No. (Table 1)	Transition	Number of configurations			
		19	51	99	201
1	$S_0 \rightarrow S_1$	296 (0.15)	337 (0.05)	339 (0.04)	340 (0.05)
	$S_0 \rightarrow S_2$	280 (0.69)	314 (0.28)	320 (0.21)	323 (0.18)
	$S_0 \rightarrow S_3$		241 (0.48)	247 (0.48)	252 (0.49)
3	$S_0 \rightarrow S_1$	286 (0.08)	309 (0.15)	309 (0.15)	319 (0.14)

[a] The transitions are characterized by the wavelength (nm) and the oscillator strength (in parentheses).

RESULTS AND DISCUSSION

The voltammograms of **I** demonstrate a two-step reduction of the compound at the Hg electrode in aqueous solution (Fig. 1). The maximum current is recorded at *ca*. 0 and –0.9 V. The first maximum most probably corresponds to reaction (1), the se-

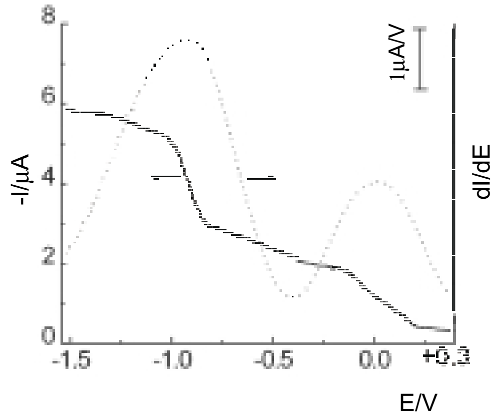
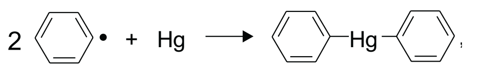


Figure 1. Integral and differential voltammograms of the 2×10^{-4} M solution of **I** in water (background electrolyte – 1 M $LiClO_4$); polarograph – Hg electrode.

cond to an unidentified electro-reduction. Furthermore, on passing through an electrolyte, the Hg drop preserves its shape, since its surface is covered with insoluble products. In order to investigate these products, electrolysis was performed on a stationary Hg electrode (the procedure is described in Experimental). Elemental analysis of the separated, dried deposit showed that it contained 42.5% C and 3.0% H. The theoretical C and H content in diphenyl is 93.50% and 6.49%, respectively, and differs from that given above. In order to assay (gravimetrically) the Hg content in the deposit, we treated it with concentrated nitric acid. The results of the analyses suggest that the main product is diphenyl mercury (the C and H contents in this compound are (%) 41.0 and 2.8, respectively), most probably formed during the reaction of diphenyl radicals adsorbed on the mercury surface with Hg atoms



(4)

It is perhaps worth noting that the formation of diphenylmercury during the reduction of phenyldiazonium salts was first observed by Nesmeyanov and Kocheshkov [20].

The electrochemical reduction of the phenyldiazonium cation was also investigated on a platinum electrode in acetonitrile solution containing $LiClO_4$ as supporting electrolyte. The concentration of the phenyldiazonium salt **(I)** was varied from 10^{-4} to 0.1 M and current-potential (I-E) curves were recorded in the potential range from 0 V to –1.5 V at sweep rates from 10 to 200 mV/s. The resolution of the reduction peaks on I-E curves turned out to be poor. A I-E dependence recorded in a 1×10^{-3} M solution of **I** at a 50 mV/s sweep rate is presented in Fig. 2. This shows that electrochemical reduction at the Pt electrode is also of a multi-step nature, as in the case of the Hg electrode. I-E curves show that reduction of **I** begins at *ca.* 0–0.4V (a very broad minimum) and continues at more negative potentials (peak near –0.8 V). The I-E curves also show that during subsequent cycles the reduction current decreases as a re-

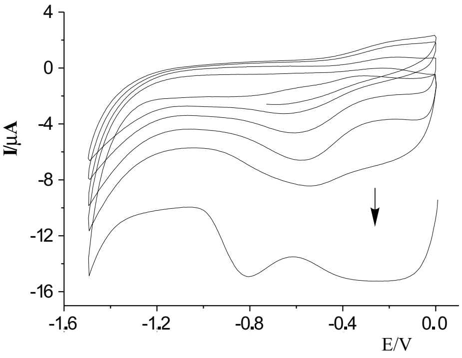


Figure 2. Cyclic voltammogram (first five scans) of the 2×10^{-3} M solution of **I** in acetonitrile (background electrolyte – 1 M $LiClO_4$); Pt electrode, sweep rate 50 mV/s.

sult of the formation of some soluble products near the electrode surface (the solution became yellowish-green).

Potentially, phenyl-*bis*-diazonium cations should exhibit an increased affinity for electrons. However, the voltammetric studies carried out in water or acetonitrile with different concentrations of **II** at different sweep rates indicated that separation of the reduction peaks is not a simple matter. In acetonitrile solution, 2×10^{-4} M of **II**, the reduction peaks are not well resolved in the first scan (Fig. 3); nevertheless, during successive scans some bends and peaks appear on the I-E curves at 0, –0.4 and –1.3 V. When the concentration of **II** is decreased to 1×10^{-4} M (Fig. 4), one redox couple can be observed during the first scan (at a formal potential of about –0.8V). In successive scans the changes in the I-E curves are probably due to the adsorption or deposition of reaction products.

All these results suggest that the reduction of phenyldiazonium and phenyl-*bis*-diazonium cations exhibits a multi-step nature. This is better demonstrated by the reduction of these cations on a mercury electrode, where the radicals may be stabilized

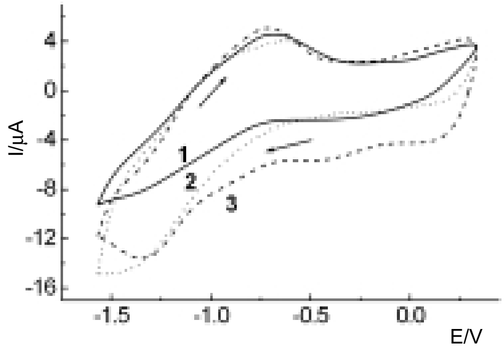


Figure 3. Cyclic voltammogram of the 2×10^{-4} M solution of **II** in acetonitrile; (1), (2) and (3) denote the 1st, 2nd and 3rd potential scan cycle, respectively (background electrolyte – 1 M solution of $LiClO_4$); Pt electrode, sweep rate 40 mV/s.

by reaction with the electrode material, and in solutions with a lower salt concentration. The multi-step reduction of methylphenyldiazonium cation on a mercury electrode has also been reported in other papers [21].

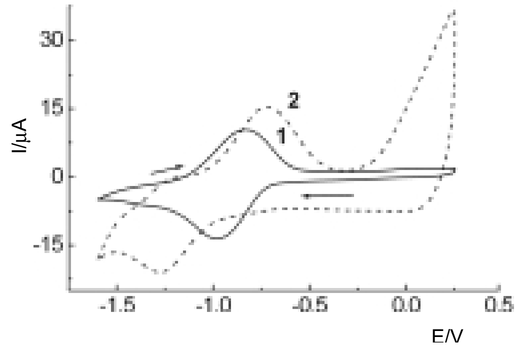


Figure 4. Cyclic voltammogram of the 1×10^{-4} M solution of **II** in acetonitrile; (1) and (2) denote the 1st and 2nd potential scan cycle, respectively (background electrolyte – 1 M solution of $LiClO_4$); Pt electrode, sweep rate 40 mV/s.

The initial solutions of **I** and **II** absorb hardly any radiation above 400 nm and are thus colorless (Figs. 5 and 6). Both compounds, however, exhibit strong absorption bands between 250–300 nm, whose position is somewhat influenced by the solvent. The long-wavelength shoulder of these bands overlaps weaker absorption, more distinct in the case of **II**, extending above 300 nm. Absorption of **II** is generally somewhat shifted towards the long wavelengths, which can be attributed to the fact that conjugation in this molecule extends over a larger number of atoms. Electrolysis of **I** and **II** in acetonitrile or water causes the solutions to become weakly yellow or greenish-yellow, which is reflected in the respective absorption spectra (Figs. 5 and 6). Noteworthy, particularly in the case of **I**, is the appearance of the absorption band at the boundary of the ultraviolet and visible region. Absorption gradually weakens

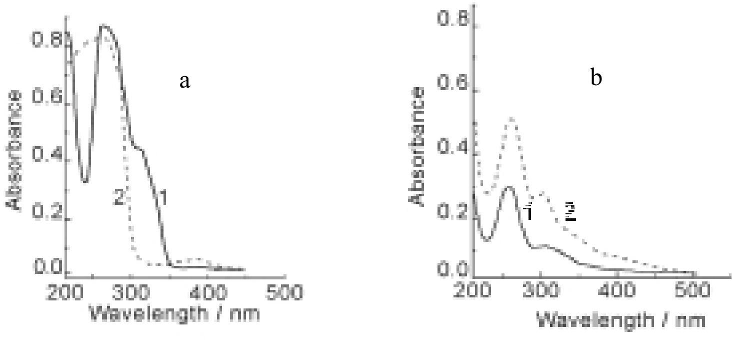


Figure 5. Electronic absorption spectra of **I** (a) and **II** (b) in acetonitrile (concentrations: 2.5×10^{-3} (**I**) and 1×10^{-2} (**II**) M) before electrolysis (1) and after the first potential scan cycle (2).

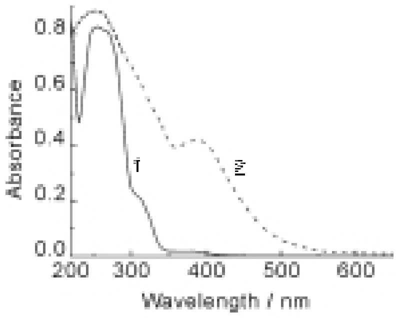


Figure 6. Electronic absorption spectra of **I** in water (concentration: 2.5×10^{-3} M) before electrolysis (1) and after the first potential scan cycle (2).

with time after electrolysis, which may indicate that the primarily generated species disappear in secondary processes.

In order to gain some idea of the origin of the electronic absorption, we compared the experimental results (Figs. 5 and 6) with the theoretically predicted transitions for selected entities (indicated in Table 1) that may be formed as a result of the recombination of products of the cathodic reduction of phenyldiazonium **(1)** and phenyl-*bis*-diazonium **(2)** cations (Table 1). In the calculations we first assumed that either azophenyl radicals, the products of primary one-electron reduction of **1** or **2**, or the radicals, which should occur if the latter species release a nitrogen molecule (reaction (2)), may participate in the recombination process. Thus, we considered compounds **3**, **4** and **5**, originating from **1** (the presence of **4** was proven following the electrochemical reduction of **1** [10]), and **6**, **7** and **8**, arising from **2**. In the case of **2**, however, its two-electron reduction can take place, as well as a one-electron reduction of products **6**, **7** and **8** formed earlier. Recombination of the radicals thus formed with the radicals originating from the one-electron reduction of **2** leads to compounds **9**, **10**, **11**, **12**, **13** and **14**, which we also took into account in our considerations. On the other hand, we did not consider the reactions of electrolysis products with the solvent, although they are known to occur [22,23]. According to the data in Table 1, absorption of radical recombination products is always expected to be long-wavelength shifted relative to that of the original cations. Moreover, long-wavelength transitions become stronger, since the respective oscillator strength takes higher values. Comparison of the predicted and experimental spectral data indicates further that the products which most probably absorb in the visible region are those resulting from the recombination of azophenyl, or azophenyl and phenyl radicals. This conclusion is in agreement with the results of our earlier investigations [9] and literature reports [10]. Two-electron reduction of **2** or one-electron reduction of **6**,**7** and **8** leads to compounds **9**, **10**, **11**, **12**, **13** and **14**, which generally absorb at longer wavelengths than the products of the one-electron reduction of **2**. This explains the broader and stronger increase of absorption in the visible region after the electrolysis of phenyl-*bis*-diazonium salts.

CONCLUSIONS

The cathodic reduction of phenyldiazonium and phenyl-*bis*-diazonium salts is a multistep process, because both the original cations and, most probably, the secondary cationic products participate in it. The appearance of absorbing visible radiation products most likely results from the recombination of two azophenyl or azophenyl and phenyl radicals. The recombination of radicals, originating from the one-electron reduction of the phenyl-*bis*-diazonium cation leads to more complex diazonium cations, whose reduction provides entities of absorption extending more broadly and strongly into the visible region.

Acknowledgments

The partial funding of this work by the Polish State Committee for Scientific Research through the Polish-Ukrainian Executive Program of Research and Technical Co-operation (grant No. PRO: III.28/1998; Contract No. 157) and DS/8000-4-0026-2 is gratefully acknowledged.

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