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# Reaction of metals with benzenediazonium tetrafluoroborate in aprotic solvents

**Research Article**

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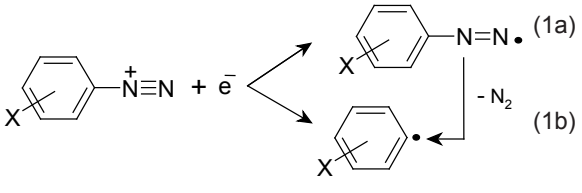
**Abstract:** The reaction of metals and glassy carbon with benzenediazonium tetrafluoroborate (BDFB) in aprotic solvents has been studied. During contact of Pt, Au, Ag, Pd, or V with glassy carbon in concentrated diazonium salt solution no change of color was observed. For Al, Ca, Cr, Cu, Fe, Ga, In, Mg, Li, Na, or Zn the process was accompanied by a rapid solution color change, rapid $N_2$ release and the loss of metal sample mass. The copper metal ionization-dissolution was studied by ultraviolet and visible absorption spectroscopy, along with gravimetric and volumetric measurements. A dissolution mechanism was proposed based on kinetic, infrared, and X-ray diffraction data. The 432 nm absorption band appearing after Cu-BDFB reaction indicates formation of the mixed complex $[Cu(N_2C_6H_5{\cdot}(N{\equiv}C\text{-}CH_3)_3]^+$ where the copper atom is covalently bonded to the azophenyl radical and coordinated to acetonitrile (ACN). This complex is thermodynamically unstable and decomposes slowly to a colorless crystalline and a black amorphous phase. The crystalline phase was identified as $[Cu(NC\text{-}CH_3)_4]BF_4$. The amorphous phase is a mixture of products formed by azophenyl and phenyl radical condensation.

**Keywords:** *Benzenediazonium tetrafluoroborate • Electrochemical reduction • Copper • Ionization-dissolution • Complexing*



## 1. Introduction

During the last 10 years diazonium-based chemistry has been used to modify carbon, metal and semiconductor surfaces. Various methods such as thermolysis, photolysis, radiolysis, and chemical or electrochemical reduction can be used to generate reactive radicals from diazonium salts. Electrochemical reduction of diazonium salts (DAS) is most often used. Reactive diazonium radicals and phenyl radicals generated according to equations [1]




can react with solvent, other phenyl radicals, and the electrode material. Reaction of the phenyl and azophenyl radicals with the initial DAS ions, and their direct and cross-recombination lead to biphenyl as well as oligomeric and polymeric products [2,3]. For example, electrochemical reduction of p-tolyldiazonium fluoroborate at a stationary mercury electrode is accompanied by the formation of p-ditolylmercury [4]. Electrochemical reduction of a wide variety of aromatic diazonium salts is a simple method to graft organic molecules to electrode surfaces. Parker et al. [5] observed blocking of Hg, Pt and Au electrodes by formation of hydrophobic films during electrochemical reduction of 1-naphthalenediazonium tetrafluoroborate in acetonitrile. Electrochemical reduction of diazonium salts can be used for the surface modification of iron and to protect it against corrosion [6].

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Carbon surface modification using diazonium salts has been the subject of extensive research. DAS directly reacts with carbon black in a protic solvent, attaching organic groups to the carbon black [7]. However, the most efficient way to modify a carbon surface is electrochemical DAS reduction. The free radicals formed by one-electron reduction are covalently bonded to the electrode surface (*e.g.* glassy carbon) as follows [8]:

$$R–C_6H_4N_2^+ + e^- \rightarrow N_2 + R–C_6H_4^{\cdot}$$
$$RC_6H_4^{\cdot} + GC \rightarrow GC–C_6H_4–R, \quad (2)$$

where R ≡ $-NO_2$, −COOH, −OH, etc. Moreover, the formation of stable, multilayered films of para-substituted DAS on a GC electrode has been reported [9,10]. A mechanism for polyphenylene film formation on electroconductive surfaces (Fe, Cu and Zn) by electrochemical reduction of benzenediazonium tetrafluoroborate in acetonitrile has been proposed by Adenier *et al.* [11].

The free radicals generated during diazonium salts' electrochemical reduction can be used to determine β-cyclodextrin [12,13]; for covalent immobilization of glucose oxidase [14]; for the modification of silicon [15−18] and carbon fiber surfaces [19], as well as single- and multi-walled carbon nanotubes [20−23]; for the surface functionalization of ultrananocrystalline diamond films [24]; for corrosion protection of steel [25]; and for surface modification of polycrystalline gold electrodes [26,27].

The modification of metal, carbon or semiconductor surfaces can be also performed without electrochemical induction. Strongly reducing properties are exhibited by carbon black [7]; clean Si surface, GaAs, Pd [28]; GC, Ni, Zn, Fe [29]; GC, Fe, Zn, Cu, Ni [30]; Fe in acidic and neutral aqueous solution of some diazonium salts ($[ArN_2^+]BF_4^-$, where Ar= $-C_6H_5$, $-C_6H_4Br$, $-C_6H_4(CH_2)CH_3$ and $-C_6H_4COOH$) [31]; Al alloy and Cu [32]; cathodically activated platinum surface [33]; and graphitic carbon [34]. Moreover, Bélanger *et al.* [35,36] have described the surface modification of carbon powder and copper electrodes by diazonium salts prepared *in situ*. The reaction of diazonium salts with transition metals results in covalent attachment of an organic group to the metal surface forming a C−Me bond [37].

Copper holds a special place in the chemistry of DAS. It is well-known that copper(I) compounds catalyze halogen substitution of the diazo group (Sandmeyer reaction) [38] and reaction of DAS with unsaturated compounds (Meerwein reaction) [39]. Moreover, as was shown early, benzenediazonium chloride forms chlorobenzene in the presence of a copper powder [1].

Although there have been many studies of electrode surface modification using DAS electrochemical reduction, some questions remain. Attention has been focused on the oxidizing agent, the products of DAS reduction and their interaction with the metal. The effect of the metal's electrochemical activity has not been studied, nor have the oxidation products and solvent effects been carefully examined. The difference between aqueous and aprotic solutions has merely been noted. DAS concentration ranges were limited to millimolar.

The aim of this work was to study the surface modification of Ag, Al, Au, Ca, Cr, Cu, Fe, Ga, In, Li, Mg, Na, Ni, Pd, Pt and glassy carbon during chemical reduction of BDFB. The results of BDFB chemical reduction were compared with electrochemical reduction. The focus was on BDFB chemical reduction by copper.

## 2. Experimental Procedure

### 2.1. Materials

Freshly distilled aniline (Linegal Chemicals, analytical grade) was used in the diazotization of aniline and purification of benzenediazonium tetrafluoroborate (BDFB), carried out according to the literature procedure [40]. Only freshly prepared benzenediazonium tetrafluoroborate (BDFB) was used.

Acetonitrile (ACN), acetone and N-methyl-2-pyrrolidone (NMP) (Aldrich) were used without further purification. Commercial grade dimethylsulfoxide (DMSO) was purified by distillation under reduced pressure (~2−3 mm Hg). Dimethylformamide (DMF) was dried over KOH and distilled from CaO.

### 2.2. Methods

An electrochemical luminescence analyzer (Physical-Technical Institute, Kharkov, Ukraine) was interfaced to a computer for data storage. A three-electrode cell with a 3.0 mm working disc electrode (glassy carbon, platinum, iron, or copper; metals purity ≥ 99.9 %) and platinum counter electrode were used. Cyclic voltammograms were scanned over (−1.2) − (0.0) V or (−1.0) − (+0.2) V *vs.* a saturated Ag/AgCl electrode at 50 mV $s^{-1}$, starting from 0.0 V. The background electrolyte was 0.1 M $LiClO_4$ (Fluka; purum p.a.) . Prior to measurement dissolved oxygen was removed by bubbling 20 min with oxygen-free argon.

UV and visible absorption spectra were recorded on a Specord M40 spectrophotometer (Carl Zeiss, Jena, Germany). The metal - BDFB reaction kinetics in solution

were studied by spectrophotometry over the ranges 220–350 and 380–680 nm, plotting absorbance *vs.* immersion time. The rate of metal dissolution-ionization in BDFB solution was studied by gravimetry.

The structure of single crystals isolated from the final reaction mixture of copper and BDFB in acetonitrile was preliminarily studied by photographic methods. Diffraction data was then recorded on a DARCh–1 single crystal diffractometer (Mo Kα-radiation, Zn β-filter, θ/2θ scan). Intensities were corrected for the Lorentz factor and polarization. The structure was solved by direct methods; light atoms were localized from Fourier difference syntheses, and the positions of the hydrogen atoms were determined from geometrical considerations. The CSD program package [41] was used for computation.

Infrared spectra of KBr pellets were recorded on a BRUKER IFS 66 spectrophotometer over 5000–400 $cm^{-1}$ (32 scans).

## 3. Results and Discussion

Chemical or electrochemical reduction of diazonium salts on metal surfaces proceeds through adsorption onto the substrate. The adsorption energy depends on the substrate surface, on the substituent and its position on the phenyl ring, the solvent, the temperature, and the electrode potential. If the C–Me bond energy and metal lattice energy are comparable, direct electron transfer from metal to adsorbate is possible with metal ionization/dissolution. Electron transfer occurs differently when the potential is applied from an external source.

The substrates can be divided into two groups. The first group of the inactive materials Pt, Au, Ag, Pd, V, and glassy carbon, while the second group comprises the active materials Cu, Al, Zn, Fe, Mg, In, Ga, alkali and alkaline-earth elements. Electrochemical polarizations of inactive and active metals differ.

The electrochemical processes were investigated by voltammetry in acetonitrile. Cyclic voltammograms (CVA) obtained on platinum and glassy carbon electrodes have a classical shape (Supplemental Figs. 1, 2). Anodic current was absent even though the potential scanning reached +0.2 V. The scan in the negative region is accompanied by a current density increase. At a Pt electrode its maximum value increased from 5.5 to 74 mA when the BDFB concentration increased from $10^{-3}$ to $10^{-1}$ M. The potential $E_p$ at the current maximum corresponds to the irreversible one-electron reduction of diazonium cation to diazonium radical shown in Eq. 1a. As noted above, these radicals can react (directly or after dediazotization to phenyl radicals) with the electrode surface forming a hydrophobic surface layer. The thickness of this organic layer increases with the number of scans, blocking the

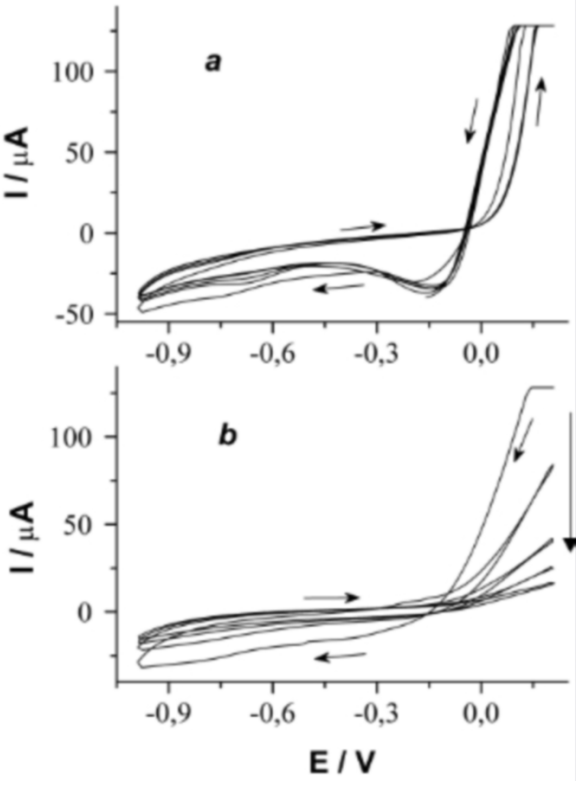



**Figure 1.** CVA of (a) 0.001 M and (b) 0.1 M BDFB acetonitrile solution at a Fe electrode with 0.1 M $LiClO_4$ background electrolyte (small arrows show scan direction; vertical arrow - the direction of current change upon sequential scanning).

reactive surface sites and decreasing the Faradic current. Bélanger *et al.* [8] observed an analogous effect during electrochemical reduction of 4-nitrobenzenediazonium tetrafluoroborate on a glassy carbon electrode. XPS analysis confirmed the formation of a 4-nitrophenyl thin film.

Cyclic votammograms of BDFB solutions on the active metal electrodes differ considerably from those on Pt. Fig. 1 presents the CVAs of BDFB solutions at an iron electrode.

For the more concentrated solution a strong anodic current occurs at +0.2 V (Fig. 1a), which does not change with the number of cycles. The decrease of anodic current at reducing potential (-0.15 V) was not observed as the number of cycles increased. Decreasing BDFB concentration to $10^{-3}$ M (Fig. 1b) leads to a sharp decrease of both anodic and cathodic currents.

Although copper is more passive than iron [42],

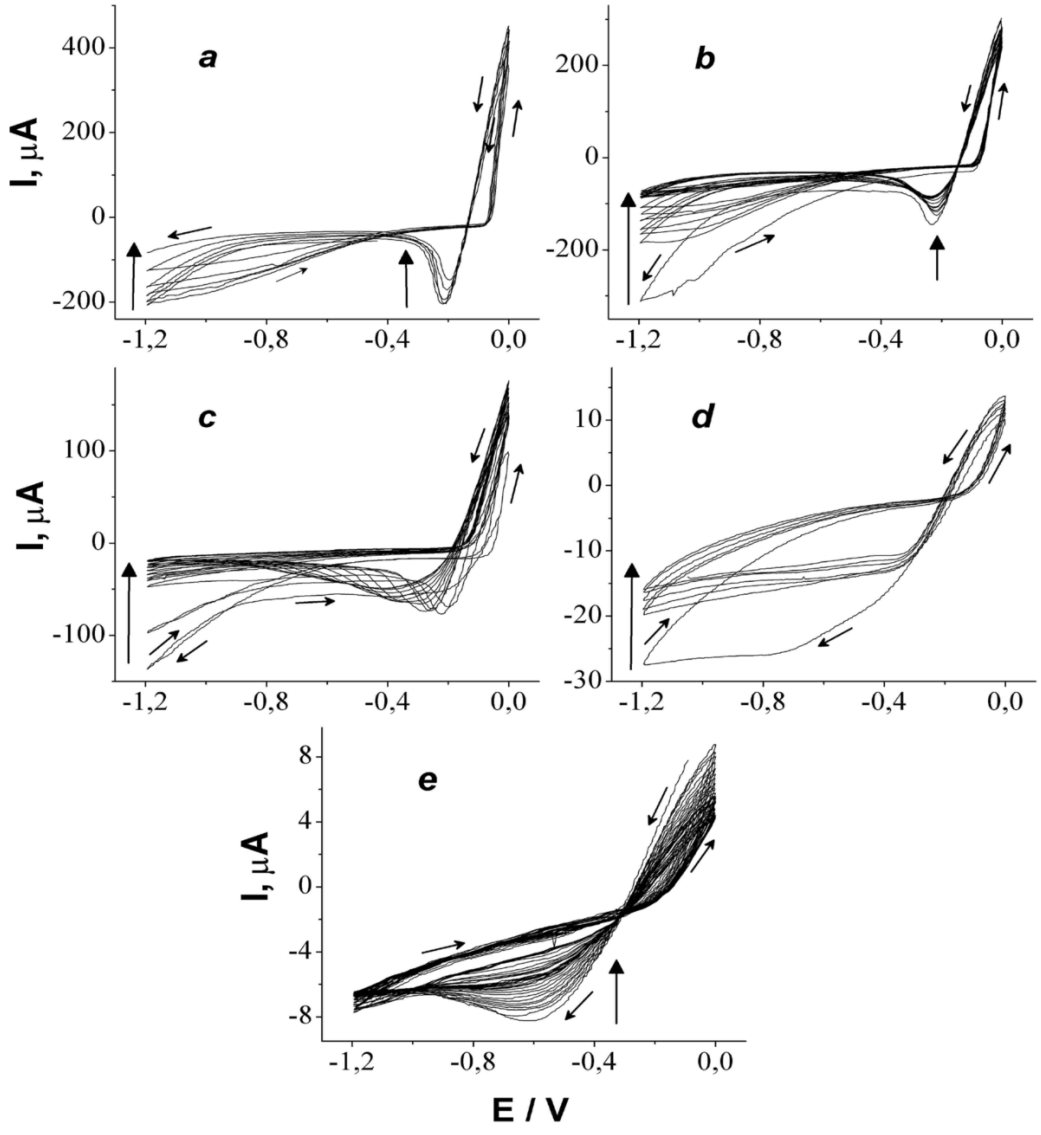



**Figure 2.** CVA of (a) 0.1 M ,(b) 0.05 M, (c) 0.01M, (d) $1\times10^{-3}$ M, and (e) $1\times10^{-4}$ M BDFB acetonitrile solution at a copper electrode (small arrows show scan direction; vertical arrow - the direction of current change upon sequential scanning).

copper and iron electrodes exhibit similar reducing properties in BDFB acetonitrile solutions (Fig. 2). At a copper electrode the anodic current at about +0.2 V is larger than that for an iron electrode.

Therefore the potential scan at the copper electrode was started at 0.0 V. The anodic peak currents were recorded; they depend on the initial BDFB concentration. Figs. 2a–2f demonstrate that the initial peak current decreases from about 450 μA to about 9 μA when the BDFB concentration decreases from $10^{-1}$ to $10^{-4}$ M.

Moreover, the anodic current strongly depends on the presence of background electrolyte ($LiClO_4$) (Supplemental Figs. 3, 4). Its presence leads to increased anodic current (increased copper dissolution-ionization rate) but also decreased cathodic current (decreased BDFB reduction rate). Therefore, background electrolyte ions are included in the structure of the electric double layer and influence the rates of diffusion and adsorption of BDFB ions as well as the dissolution-ionization process.

The BDFB electrochemical reduction is irreversible, confirmed by the absence of an oxidation current during

the reverse scan. The observed high anodic currents correspond to the ionization-dissolution of copper and iron:

$$Fe^0 \rightarrow Fe^{n+} + n\,e^-; \quad (3)$$
$$Cu^0 \rightarrow Cu^{n+} + n\,e^-,$$

Scanning of the electrode potential in the cathodic region leads to a current inversion and the appearance of a cathodic current maximum, which corresponds to BDFB reduction. The screening of the Cu and Fe electrode surfaces by the products of the BDFB reduction is only partial, because the cathodic current decrease is smaller than for inert electrodes. Moreover, the anodic current maximum due to copper ionization-dissolution does not disappear.

It should be noted that intense dissolution-ionization of Fe, Cu [43,44], Mg [44] and Zn, Ni and Al [45] have also been observed in the absence of electrode polarization when [DAS] ≥ 0.05 M. Their chemical corrosion is due to the strongly oxidizing properties of the phenyl diazonium cations and their adsorption on the metal surface. Thus, the decision to study metal ionization-dissolution in more detail was made.

**Table 1.** Color of 0.1 M BDFB in acetonitrile after contact with metal sheet for 4 h (initial color = light yellow)

| Metal phase | Solution Color | Metal | Solution Color |
|---|---|---|---|
| Fe | Intense red | In | Light yellow |
| V | Light yellow | Ga | Green |
| Pd | Dark yellow | Mg | Orange |
| Pt | Light yellow | Al | Yellow-green |
| Ni | Pink | Na | Dark red* |
| Ag | Light yellow | Li | Green* |
| Au | Light yellow | Ca | Red |
| Cr | Light-green | Cu | Intense red |

* intense gas evolution

**Table 2.** Corrosion (ionization-dissolution) rate of copper in acetonitrile at different BDFB concentrations.

| C(DAS) / M | Corrosion rate / μmol cm$^{-2}$ min$^{-1}$ |
|---|---|
| 0.05 | $6.047\times10^{-2}$ |
| 0.10 | $19.805\times10^{-2}$ |
| 0.15 | $40.223\times10^{-2}$ |
| 0.20 | $80.966\times10^{-2}$ ($354.4\times10^{-2}$*) |

*for second leg of curve 6 (see Fig. 3b)

During metal dissolution the light yellow BDFB solution changes color, while color constancy indicates that no reaction occurred. These effects (acetonitrile solvent) are presented in Table 1. V, Pt, Ag and Au do not react with BDFB solution, as the color is unchanged.

Quantitative results of the transformations in the DAS-metal system were obtained by measuring the weight loss of the metallic sheet as a function of immersion time in BDFB solution. Larger losses were observed at higher BDFB concentrations. Copper dissolutions in different BDFB concentrations in acetonitirile and acetone are presented in Fig. 3. As shown in Table 2, a 4x increase in BDFB concentration leads to a 13x (or 58x for the later stage of corrosion) increase in dissolution rate.

The influence of the solvent on ionization-dissolution was studied using Cu sheets (area 2 cm$^2$). Dissolution of copper takes place only in aprotic media, while in aqueous, butylacrylate and ethanol−water solutions no change of initial BDFB solution color or copper weight was observed (Supplemental Fig. 5). For the same BDFB concentrations the maximum corrosion rate was observed in acetonitrile and the minimum in NMP.

The process of was also studied *in situ* by UV-visible absorption spectroscopy. The metal sheet was placed in a quartz cuvette containing BDFB solution. Absorption

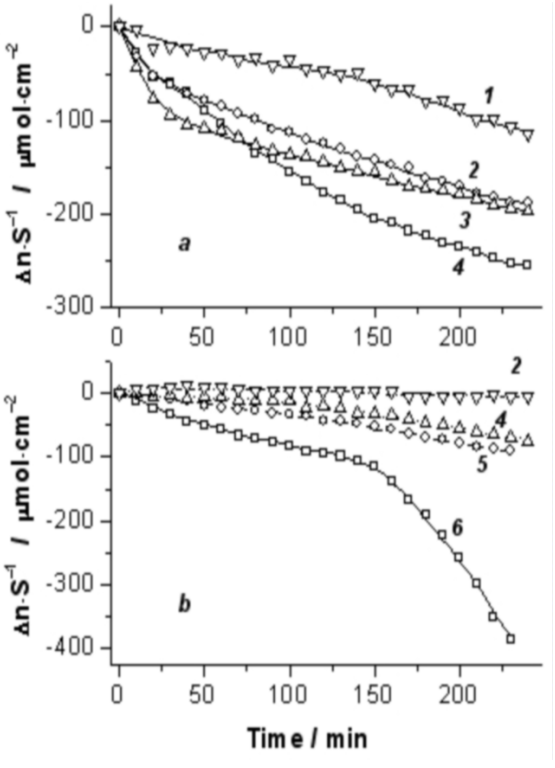



**Figure 3.** Dependence of the dissolved Cu (in μmol cm$^{-2}$)vs. time in BDFB solutions in (a) acetone and (b) acetonitrile for [BDFB]: 1- 0.025 M; 2 - 0.05 M; 3 - 0.075 M; 4 - 0.10 M; 5 - 0.15 M; 6 - 0.20 M.

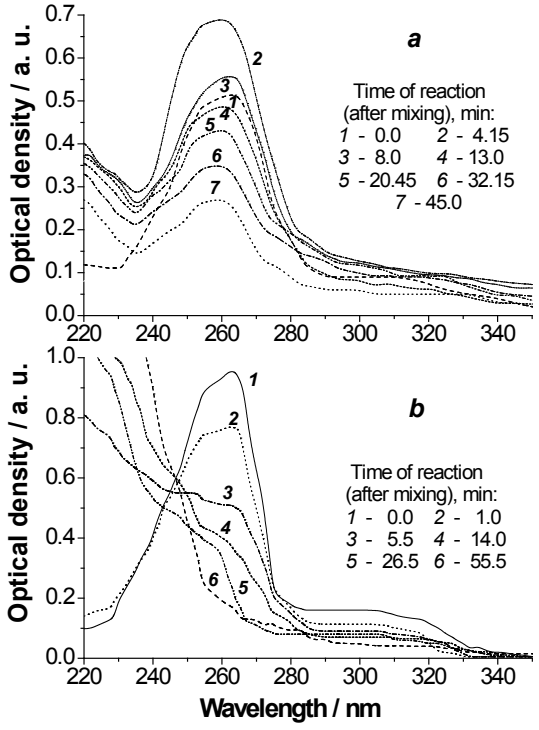



**Figure 4.** Evolution of absorbance (220-360 nm) of $5\times10^{-4}$ M BDFB in (a) ethanol and (b) acetonitrile during contact with copper sheet (0.0 min = initial DAS solution).

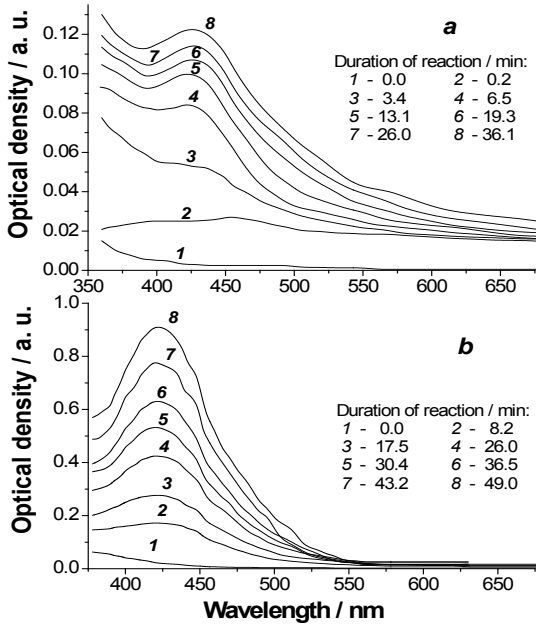
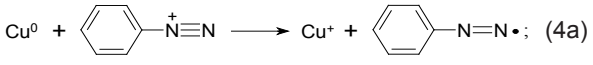



**Figure 5.** Evolution of absorbance (360-700 nm) of the BDFB acetonitrile solution during contact with copper sheet for [BDFB]: (a) 0.02 M and (b) 0.1 M (0.0 min = initial DAS solution).

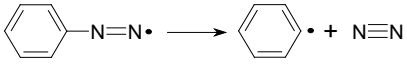
maxima at 260 and 262 nm were observed in acetonitrile and ethanol, respectively (Figs. 4a–4b). The intensity of these bands decreases with time in the presence of copper, while in the presence of zinc or iron the intensity of the band increases (Supplemental Fig. 6).

If the decrease of intensity can be explained by the decrease in [BDFB] by reaction with the copper, the increase in band intensity in the case of Zn or Fe is due to reaction products which absorb light in same region as BDFB. At the same time, a new band with a maximum in the 420–432 nm range (Fig. 5) arises. It is attributed to these reaction products because its intensity increased with time. In our opinion this band is due to a complex of copper in a low oxidation state, analogous to the complex of Cu(I) and o-phenanthroline [46].

The diazo group bonded to a benzene ring $[Ar-N\equiv N]^+$ is a unique formation with an unusual electron density distribution. The high reactivity of diazonium salts, including with metals, is well known. Oxidative metal ionization-dissolution in aprotic solutions is caused by the very positive DAS standard reduction potential. The rate of this heterogeneous reaction depends on the contact area; replacement of the metal sheet by powder leads to a sharp increase in reaction rate. Complete dissolution of the Cu sheet (thickness = 0.5 mm) in concentrated solution ([BDFB] ≥ 0.25 M) was observed after 8–10 hours, while the same reaction using an equivalent quantity of Cu powder was complete in 10 minutes. The BDFB reaction with copper is accompanied by intense gas evolution, beginning immediately after mixing. The process slows as the BDFB solution is exhausted. On the other hand, if copper powder is used with a stoichiometric excess of BDFB (initial molar ratio Cu : BDFB = 0.7 : 1), only 70% of the metal reacted with BDFB, although BDFB was not detected in the final solution. Moreover, according to the volume of evolved nitrogen 68.7% of the BDFB reacted with copper. Thus only ~70% of the initial BDFB dediazotized during reduction by metallic copper:

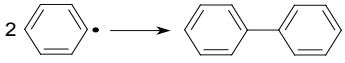



(4a)



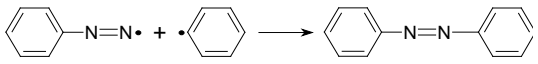
(4b)

As noted above, the formed radicals can also react with each other. The products of direct or cross-recombination of phenyl and azophenyl radicals are biphenyl



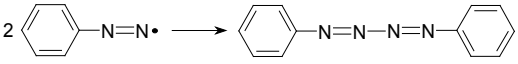
(5)

azobenzene




(6)

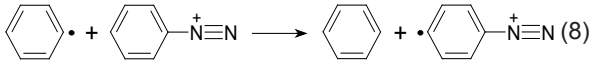
and diazobenzene




(7)

Cohen *et al*. [47] detected the dimeric analogs of biphenyl and azobenzene during the reduction of 4-nitrobenzenediazonium tetrafluoroborate by tetrakis(acetonitrile)copper(I) perchlorate in acetonitrile. The formation of azobenzene and diazobenzene explains why ~30% of the initial BDFB does not take part in dediazotization. Moreover, the highly reactive phenyl radicals can abstract hydrogen from solvent, forming benzene. This reaction proceeds slowly in acetonitrile due to the low mobility of methyl hydrogen atoms. However, Ar–H forms in 30% yield when tetrahydrofuran is used [35].

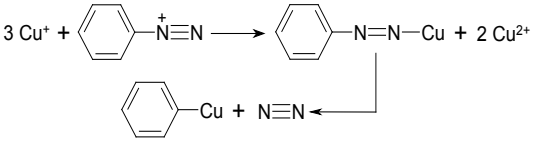
Another possibility is the reaction of phenyl radicals with the initial benzenediazonium cations. For example, phenyl radicals can abstract the DAS cation para-hydrogen




(8)

leading to polymer formation [2].

Reaction of DAS with Cu(I) cations formed in Reaction 4 yields arylcopper:




(9)

Cohen *et al*. [47] have shown that high Cu(I) concentrations favor azobenzene formation, while high concentrations of Cu(II) and phenyldiazo cations yield mainly biphenyl. On the other hand, Cu(I) ions easily form complexes: mononuclear complexes of Cu(I) with acetylene [48]; propargyl alcohol [49]; 4,5-dimethyl-2-phenylphospharin [50]; and styrene [51]; as well as binuclear complexes with 1,2,4-triphospholil [52], and azophenine [53] have been reported and their crystal structures determined. Therefore the complexation of Cu(I) with DAS ions in aprotic solvents must be taken into account. The nitrogenated components of the reaction mixture, *i.e*., solvent (ACN) and the nitrogen-containing products of the DAS reduction (azo- and diazobenzenes) can be ligands in such complexes. To determine the mechanism of copper ionization-dissolution during oxidation by BDFB, we decided to examine the reaction products.

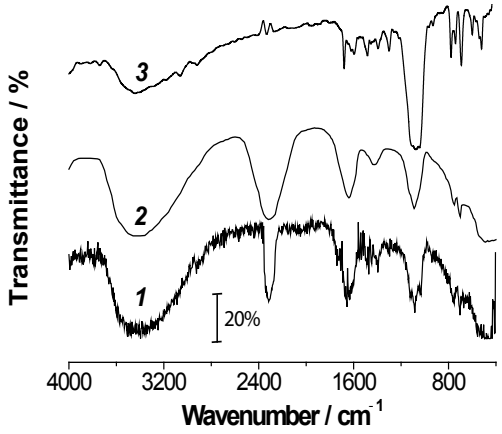



**Figure 6.** IR spectra of (1) initial BDFB; and products of copper reaction with BDFB in acetonitrile (after solvent evaporation) (2) on the copper sheet surface; (3) amorphous phase.

The IR spectra of the initial BDFB and the products formed on the Cu surface do not differ significantly, in spite of the visible changes (Supplemental Fig. 7). The diazo group vibrations in BDFB occur at 2290 $cm^{-1}$. The diazo group transforms during reduction, either by dediazotization or by formation of an azo group, *i.e*., it is not among the reaction products. As seen in Fig. 6 (spectrum 2), a band at 2290 $cm^{-1}$, though somewhat narrowed, is also present in the spectrum of the product. However, the 2290 $cm^{-1}$ band is not unique, as nitriles, isocyanates and isocyanides also absorb in this region [54]. The band at 1050 $cm^{-1}$, analogous that of BDFB, confirms the presence of $BF_4^-$ in the products. The 1610–1660 $cm^{-1}$ band may be attributed to the azo group ($\nu_{N=N}$); however, C=N vibrations appear in the same region. Thus, acetonitrile and $BF_4^-$ ions may be present in the reaction products between BDFB and copper. Further, there is no 2290 $cm^{-1}$ absorption band in the product of BDFB reduction by lithium, indicating that unreduced diazo groups and acetonitrile are absent.

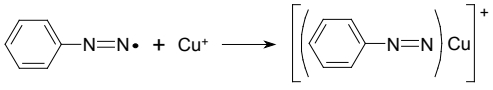
After 24 hours of copper dissolution the reaction mixture was homogeneous. During slow evaporation of the solvent at room temperature light yellow transparent crystals precipitated and a suspension with a dark red dispersed phase formed. After complete solvent evaporation a mixture of amorphous and crystalline phases remained. The thin coating of amorphous phase was removed from the largest crystals, which were studied by IR and X-ray diffraction. Separation of the dispersed phase was not successful because small crystals could not be removed. Therefore there are few differences between the IR spectra of amorphous (Fig. 6, spectrum 3) and crystalline (Supplemental Fig. 7) phases. The main difference concerns the

band position and intensity in the 680−850 and 1300−1625 $cm^{-1}$ regions. The amorphous phase 1600 $cm^{-1}$ band is due to the azo group, while the 1300 and 1390 $cm^{-1}$ bands present in the spectra of both the crystalline and amorphous phases can be attributed to the $\delta_{C-N}$.

A well-shaped crystal (5×2×1 mm) was subjected to X-ray diffraction. The chemical composition, crystal lattice (space group) and atomic parameters were determined (see Supplemental Table 1). The structural subunit is the known complex $Cu(N{\equiv}C\text{-}CH_3)_4{\times}BF_4$ [56] (Supplemental Fig. 8). This is in good agreement with the IR data (Supplemental Fig. 7), where acetonitrile and tetrafluoroborate anions were identified.

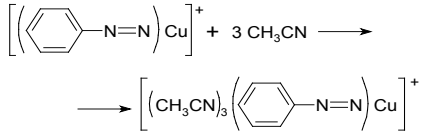
The formation of a four-coordinate Cu(I) complex requires comment. Based on studies of electrochemical dissolution of copper in monoethanolamine, where the complex $[Cu^{II}(MEA)_4]^{2+}$ forms (MEA−monoethanolamine), Shih *et al*. concluded that tetrahedral coordination is typical for Cu(II). $[Cu^{I}(MEA)_2]^{+}$, with coordination number two, was found for Cu(I) [58,59]. A coordination number of two was also observed for the complex of Cu(I) with 2,9-dimethyl-1,10-phenanthroline [60]. However, well-studied tetrahedral Cu(I) complexes also exist. For example, the complex $Cu(NCCH_3)_4ClO_4$ is formed between Cu(I) cations and acetonitrile [57].

The complex $Cu(N{\equiv}C\text{-}CH_3)_4{\times}BF_4$ is the final crystalline product of copper dissolution during oxidation by BDFB. In our opinion, the first stage is the formation of a mixed Cu(I) complex, where azophenyl radicals are in the coordination sphere along with acetonitrile. Its formation can be represented by the following:




(10)

Because this reaction proceeds in acetonitrile, $CH_3CN$ molecules react with azophenyl copper to form a complex with its coordination sphere completed to 4:




(11)

This complex is unstable and decomposes to crystalline ($Cu(CH_3CN)_4BF_4$) and an amorphous phase, the latter being a mixture of dimeric and oligomeric nitrogenated organic compounds. This mechanism of copper dissolution via intermediate formation of mixed azophenyl acetonitrile Cu(I) complexes correlates well with the experimental observation of partial BDFB dediazotization (70%) during reaction with copper powder.

The formation of Cu(I) mixed complexes was observed by Parsons *et al*., who isolated and identified $Cu_3(dpphp)_2(CH_3CN)_{1.7}(CH_2Cl_2)_{0.3}]ClO_4$ complex (where dpphp − 6-diphenylphosphino-2-hydroxy-pyridine) [61].

## 4. Conclusions

Free radical generation during DAS electrochemical reduction is widely applied both in synthesis and for surface modification of metallic and non-metallic substrates. However, this process was not successful for the modification of a copper surface, especially under [BDFB] ≥ 0.05 M. High anodic currents due to ionization-dissolution of the metal were observed during contact of a copper electrode with the BDFB aprotic solution. Depression of the anodic current occurs only at potentials more negative than −0.5 V (*vs.* sat. Ag/AgCl). Electrochemical dissolution also takes place for Zn, Fe, and Mg; and partially for Ni and Ag, but only in aprotic solvents. Metal ionization-dissolution does not occur in water except for alkaline and alkaline-earth metals. Dissolution is accompanied by intense gas ($N_2$) evolution and a rapid change of solution color.

Copper ionization-dissolution in BDFB aprotic solutions was studied by spectrophotometric, gravimetric and volumetric methods. The absorption band at 260 nm due to BDFB decreases with time. A new band around 430 nm appears; its intensity increases with prolonged contact between metallic copper and solution. Its precise position, form and height depend on the solvent, *i.e.*, maxima are observed at 427, 423 and ~330−320 nm in ACN, NMP and acetone (ethanol), respectively. This band can be attributed to an intermediate complex of Cu(I), *i.e.*, $[Cu{-}(N{=}N{-}C_6H_5)(N{\equiv}C{-}CH_3)_3]^{+}BF_4^{-}$, where Cu is coordinated to three solvent molecules and forms a chemical bond with the azophenyl group. This complex decomposes slowly with the formation of crystalline $[Cu(N{\equiv}C{-}CH_3)_4]BF_4$ and an amorphous phase. The latter is a mixture of oligomers containing phenyl and azophenyl fragments. Volumetric studies indicated that only 70% of the initial BDFB dediazotized during the reduction by metallic copper. The rest of the BDFB (~30%) was reduced to azophenyl radicals by an inner sphere mechanism. This result can be explained by competing reactions of the Cu(I) ions with the initial diazonium salt and intermediates. Moreover, phenyl radical recombination produces the biphenyl found in solution. The products of phenyl radical deactivation must be also considered.

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