

Products of the interaction of copper and benzenediazonium tetrafluoroborate in acetonitrile medium

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The products of the chemical interaction of copper and a concentrated (≥ 0.05 M) benzenediazonium tetrafluoroborate (BDFB) solution in acetonitrile have been studied. It is proposed on the base of the obtained results that the intermediate of the copper dissolution-ionization, which corresponds to an absorption band with a maximum at 432 nm, is the mixed complex $[\text{Cu}(\text{N}\equiv\text{N}-\text{C}_6\text{H}_5)(\text{N}\equiv\text{C}-\text{CH}_3)_3]^+$, which contains three acetonitrile molecules and the copper ion covalently bonded to an azophenyl radical. This complex is thermodynamically unstable and decomposes slowly into a colorless crystalline and a black amorphous phase. The crystalline phase was identified as $[\text{Cu}(\text{N}\equiv\text{C}-\text{CH}_3)_4]^+\text{BF}_4^-$ by X-ray diffraction, while the amorphous phase is a mixture of oligomeric products of different lengths, which are formed as the result of the condensation of azophenyl and phenyl radicals.

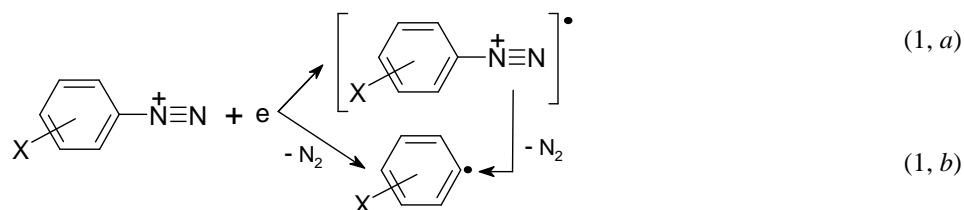
Copper / Benzenediazonium tetrafluoroborate / Acetonitrile / Dissolution-ionization / Cu(I) complexes / Crystal structure

Introduction

During the last 10 years, the salts of arenediazonium (DAS) have been used to modify carbon materials, metal, indium-tin oxide (ITO) and semiconductor (Si, GaAs) surfaces [1]. Such materials, functionalized by organic mono- or multilayers, are widely applied in the development of chemically modified stationary phases for electrochemically modulated liquid chromatography [2]. The modification of a diamond surface by reduction of DAS is used in the design of a universal composition platform for the immobilization of chemical and biological components [3] and for

Suzuki reactions in the surface layer [4]. In addition, DAS can be the initial materials for the design of spatially assembled molecular structures, which makes it possible to study the phenomena that are the basis of molecular and optical electronics [5,6].

Various methods can be used to generate reactive intermediates from diazonium salts, for example electrochemical reduction, thermolysis, photolysis, radiolysis, or chemical reduction. Reduction of the aryldiazonium cation (DAC) involves the generation of a reactive diazonium radical, or the cleavage of nitrogen and formation of a phenyl radical, according to the equations [7]:



The free radical particles produced in this way can react with the solvent, other phenyl radicals and the electrode material. The interaction of the phenyl and azophenyl radicals with the initial aryldiazonium cations, as well as their direct and cross-recombination, lead to the formation of biphenyl, oligomeric and polymeric adducts [8,9], while the electrochemical reduction of *p*-tolylidiazonium tetrafluoroborate on a stationary mercury electrode is accompanied by the formation of *p*-ditolylmercury [10]. Ahlberg *et al.* observed the blocking of Hg, Pt and Au electrodes by the formation of hydrophobic films during the electrochemical reduction of 1-naphthalenediazonium tetrafluoroborate in acetonitrile [11]. The strategy of the electrochemical reduction of a wide variety of aromatic diazonium salts can be used for the modification of the surfaces of iron [12] and carbon materials [13-16]. Moreover, Belanger *et al.* have described the *in situ* modification of carbon soot and copper electrodes during the synthesis of the corresponding diazonium salts without their isolation [17,18].

The diazo-group bonded to the benzene ring $[\text{ArN}=\text{N}]^+$ is a unique formation with a specific distribution of electron density, that determines the high reactivity of DAS in different chemical reactions. Because of the strong oxidative potential the aryldiazonium cations also react directly (without any electrochemical induction) with both metallic and carbon surfaces, which leads to the formation of C–Me or C–C(substrate) covalent bonds [2,19-23]. However, the intensive dissolution-ionization of Cu [24-26], Mg [25], Al, Zn and Ni [27] proceeds simultaneously with the modification of the surfaces in concentrated (≥ 0.05 M) DAS aprotic solutions. On account of the specific properties of copper, which catalyzes aggregate reactions with DAS participation [7,28,29], we studied the products of the chemical interaction of benzenediazonium tetrafluoroborate (BDFB) with copper in details, which gave us the possibility to propose a mechanism for this process.

Experimental

Freshly distilled aniline (Linegal Chemicals, analytical grade) was used for the synthesis of benzenediazonium tetrafluoroborate (BDFB). The diazotiation of aniline and purification of the product were carried out following well-known procedures [30]. Only freshly prepared benzenediazonium tetrafluoroborate was used in all the experiments. Acetonitrile (ACN) (Merck KgaA, LiChrosolv[®], $\geq 99.8\%$, isocratic grade for liquid chromatography, content of water $\leq 0.05\%$) was used without further purification. The purity of copper (foil with thickness 0.5 mm (Sigma-Aldrich) and high-dispersed powder) was 99.98 wt.%.

All the experiments were carried out at room (20°C) temperature.

Infrared spectra were recorded on a BRUKER IFS 66 spectrophotometer over the 5000-400 cm^{-1} range. All spectra were collected with an accumulation of 32 scans.

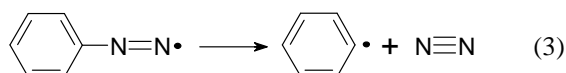
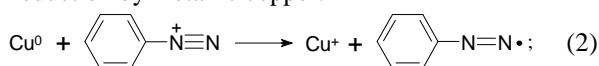
The structure of single crystals isolated from the final reaction mixture of the interaction of copper and BDFB in an acetonitrile solution, was preliminarily studied by photographic methods. Diffraction data was then recorded on a single crystal diffractometer DARCh-1 (Mo $K\alpha$ -radiation, Zn β -filter, $\theta/2\theta$ scan) and used to determine the structure. The intensities were corrected for the Lorentz factor and polarization. The structure was solved by direct methods; the light atoms were localized from Fourier difference syntheses, and the positions of the hydrogen atoms were determined from geometrical considerations. The CSD program package [31] was used for the computations.

Results and discussion

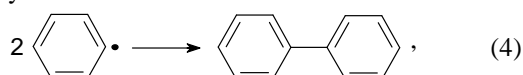
Reduction of diazonium salts on carbon, semiconductor or metal surfaces proceeds through a preliminary stage of chemisorption that leads to the formation of a covalently grafted mono- or multilayer on the substrate surface. The interaction energy of the adsorption complex depends on the type and the state of the electrode surface, on the nature and position of the substituent group in the phenyl ring of the diazonium salt, the solvent type and temperature. If the C–Me bond energy and the metal lattice energy are comparable, direct electron transfer from the electrode to the particles of the adsorbate is possible. This leads to ionization/dissolution of the metal. In a different way, electron transfer takes place only when a potential is applied from an external source. The adsorbents can be divided into two groups from this point of view [24]. The first group consists of “inactive” materials, such as Pt, Au, Ag, Pd, V, or glassy carbon, while the following “active” materials: Cu, Al, Zn, Fe, Mg, In, Ga, alkali and alkaline-earth elements belong to the second group. The electrochemical polarization of inactive and active metals is different.

The phenomenon of ionization-dissolution of metals in aprotic DAS solutions is determined by the strong oxidative properties of DAC. The rate of this heterogeneous reduction of DAC depends on the contact area of the metallic phase and the BDFB solution. Therefore the replacement of the metal sheet by fine-dispersed metal powder leads to a sharp increase of the reaction rate. Complete dissolution of the Cu sheet was observed after 8-10 hours, whereas the same reaction using an equivalent quantity of Cu powder was completed after 10 minutes. The reaction of BDFB with copper is accompanied by an intense gas evolution, which begins immediately after the addition of the DAS solution to the copper powder. Then this process slows down as the result of the

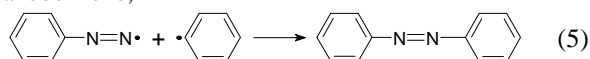
exhaustion of the DAS solution. In the case when copper powder was used, the part of metal that had reacted with DAS was only 70% using a stoichiometric excess of DAS solution (the initial molar ratio Cu : DAS was equal to 0.7 : 1), although no DAS was detected in the final solution. Moreover, according to the volume of evolved nitrogen the amount of DAS that had reacted with copper was 68.7%. Consequently it was assumed that only ~70% of the initial BDFB had dediazotized during the reduction by metallic copper:



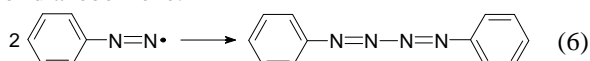
These radicals can react with each other, with a metallic surface, the solvent or initial DAS. The products of the direct or cross-recombination of the phenyl and azophenyl radicals are, respectively, biphenyl



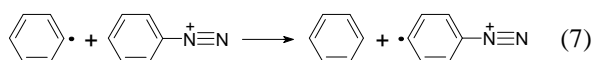
azobenzene,



or diazobenzene.

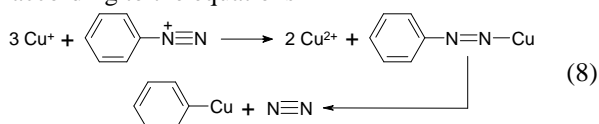


Cohen *et al.* detected dimeric products, exactly biphenyl and azobenzene type, during the reduction of 4-nitrobenzenediazonium tetrafluoroborate by tetrakis(acetonitrile)copper(I) perchlorate $(\text{CH}_3\text{CN})_4\text{Cu}^+\text{ClO}_4^-$ in acetonitrile [32]. The formation of azobenzene and diazobenzene explains the experimental observation that ~30% of the initial DAS does not take part in the dediazotization reaction. The highly reactive phenyl radicals can eliminate hydrogen from solvent molecules with the formation of benzene. This reaction proceeds slowly in acetonitrile, due to the low mobility of the hydrogen atoms in the methyl group. However, Ar-H forms with a 30% yield when another solvent is used, for example tetrahydrofuran [17]. Another possible reaction is the interaction of phenyl radicals with the initial benzenediazonium cations. For example, the phenyl radicals can eliminate the hydrogen in the *para*-position of the DAS cation.



Moreover, these reactions can lead to the formation of oligomeric or polymeric products [8].

The interaction of DAS with Cu(I) cations formed in reaction (2) involves the formation of arylcopper according to the equations



Cohen *et al.* showed that high concentrations of Cu(I) ions favor the formation of azobenzene, while for high concentrations of Cu(II) and phenyldiazonium cations, mainly biphenyl is formed [32]. On the other hand, Cu(I) ions easily form complexes with different ligands. For example, mononuclear complexes of Cu(I) with acetylene [33], propargyl alcohol [34], 4,5-dimethyl-2-phenylphospharin [35], styrene [36] and binuclear complexes with 1,2,4-triphospholil [37], and azophenine [38] have been reported and their crystal structures determined. Therefore the possibility of complexation must be taken into account during reactions of Cu(I) ions in aprotic solution. The nitrogenated components of the reaction mixture, *i.e.* the solvent molecules (ACN) and the undenitrated products of the DAS reduction (azo- and diazobenzenes) can be the ligands in such complexes in the studied system. In the system investigated here the initial light-yellow DAS solution rapidly changed color to red after the contact with metallic copper. In our opinion the strong color saturation of the solution indicates complexation in the system. Earlier studies carried out *in situ* by UV-visible absorption spectroscopy have shown that an absorption band with a maximum at 260 nm corresponds to the initial BDFB solution in acetonitrile [24]. The intensity of this band decreases with time in the presence of copper, which can easily be explained by the decrease of the concentration of DAS, as the result of its interaction with the copper sheet. In the same time, a new band with a maximum in the 420-432 nm region arises in the spectrum [24]. It can be attributed to products of the interaction between BDFB and the metal because its intensity increases with time. In our opinion this absorption band corresponds to a complex of copper in low oxidation state, analogous to the complex of Cu(I) and *o*-phenanthroline [39].

In order to determine the mechanism of copper ionization-dissolution during the oxidation of copper by BDFB, we decided to study in detail the reaction products, namely the organic layer and the amorphous and crystalline phases that formed, respectively, on the surface of the copper sheet and in the volume of the reaction system after partial evaporation of the solvent. The IR spectra of the initial DAS and of the product formed on the surface of the Cu sheet do not differ significantly, in spite of the visible changes in the reaction system (Fig. 1). The valence vibrations of the diazo-group in the initial DAS correspond to an absorption band with a maximum at 2290 cm^{-1} . The diazo-group transforms during the DAS reduction, either by dediazotization or by the formation of an azo-group, *i.e.* it is not among the reaction products. However, as seen in Fig. 1 (spectrum 2), a band at 2290 cm^{-1} , though somewhat narrowed, is also present in the spectrum of the undissolved reaction product. This observation can be explained by the fact that a band with a maximum at 2290 cm^{-1} is not unique, but also nitriles, isocyanates and isocyanides absorb in this spectral region [40]. The band at 1050 cm^{-1} , which

is analogous to the band in the spectrum of the initial BDFB, confirms the presence of BF_4^- ions in the reaction products. The band in the region $1610\text{--}1660\text{ cm}^{-1}$ may be attributed to vibrations of the azo-group ($\nu_{\text{N}=\text{N}}$), however the vibrations of $\text{C}=\text{N}$ groups appear in the same region. These facts lead to the conclusion that solvent molecules (ACN) and BF_4^- ions may be present in the mixture of the products of the interaction of DAS with copper.

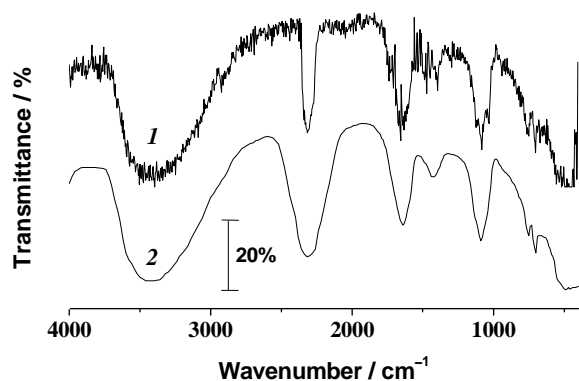


Fig. 1 IR spectra of initial BDFB (1) and the product (2) formed on the surface of a copper sheet after interaction with a BDFB acetonitrile solution.

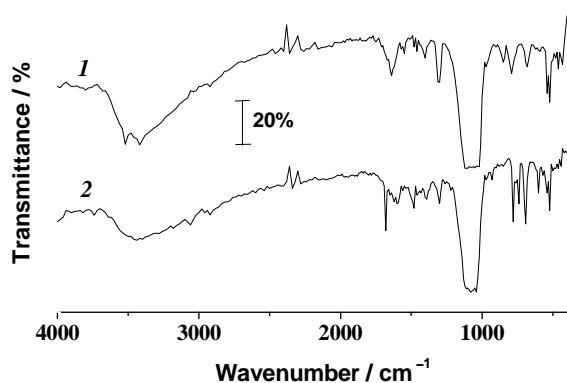


Fig. 2 IR spectra of the crystalline (1) and amorphous (2) phases that were observed after complete evaporation of the solvent from the reaction mixture of BDFB and copper powder in acetonitrile.

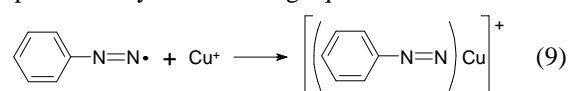
After 24 hours of copper dissolution the reaction mixture was homogeneous. However, light yellow transparent crystals precipitated from the solution and a suspension with a red-brown (black after complete drying) dispersed phase formed during slow spontaneous evaporation of the solvent at room temperature. After complete evaporation of the solvent a mixture of amorphous and crystalline phases had formed in the system. The largest crystals were

cleaned from the thin coating of amorphous phase and then studied by IR spectroscopy and X-ray diffraction. The separation of the dispersed phase was not successful because this amorphous phase always contained small crystals of the crystalline phase. Therefore there are few differences between the IR spectra of the crystalline and amorphous phases (Fig. 2). The main difference concerns the position and intensity of the absorption bands in the $680\text{--}850$ and $1300\text{--}1625\text{ cm}^{-1}$ wave number regions. The absorption band of the amorphous phase at 1600 cm^{-1} is connected with the vibration mode of the azo-group, while the bands at 1300 and 1390 cm^{-1} are present in the spectra of both the crystalline and amorphous phases and can be attributed to deformation vibrations $\delta_{\text{C-N}}$ [41]. Taking into consideration the results of previous studies of products of DAS electrochemical reduction [8,42], it may be argued that the amorphous phase is a mixture of oligomeric nitrogen-containing organic compounds, which form as the result of the condensation of azophenyl radicals and products of their decomposition.

A well-shaped crystal ($5\times 2\times 1\text{ mm}$) was used for X-ray diffraction studies. From the data collected on a single-crystal diffractometer the chemical composition, the crystal lattice (space group) and the atomic parameters were determined (see Table 1). It was found that the structural subunit of the crystal is the already known complex $\text{Cu}(\text{NCCH}_3)_4\cdot\text{BF}_4$ [43] (Fig. 3) The crystal structure is in good agreement with the IR absorption spectroscopy data (Fig. 2), where acetonitrile and tetrafluoroborate anions were identified.

The formation of a four-coordinated Cu(I) complex requires some comments. Shih *et al.* [44,45] concluded, based on studies of the electrochemical dissolution of copper in monoethanolamine, where the complex $[\text{Cu}^{\text{II}}(\text{MEA})_4]^{2+}$ forms (MEA – monoethanolamine molecule), that tetrahedral coordination of ligands is typical for Cu(II) ions. A complex with coordination number two, namely $[\text{Cu}^{\text{I}}(\text{MEA})_2]^+$, was found for the ions Cu(I). Coordination number two was also observed for the complex of Cu(I) with 2,9-dimethyl-1,10-phenanthroline [46]. However, well studied complexes of Cu(I) with tetrahedral coordination of ligands also exist. For example, the complex $\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$ is formed between Cu(I) cations and acetonitrile ligands [47].

The complex $\text{Cu}(\text{CH}_3\text{CN})_4\cdot\text{BF}_4$ is the final crystalline product of the copper dissolution during oxidation by DAS. In our opinion, the first stage is the formation of a mixed Cu(I) complex, where azophenyl radicals, in addition to acetonitrile molecules, are in the coordination sphere. Its formation can be represented by the following equations:



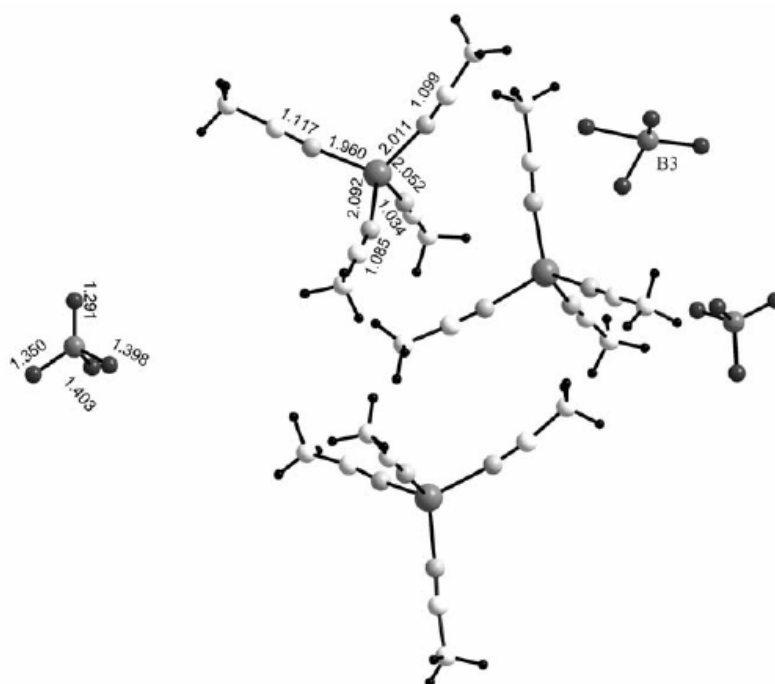
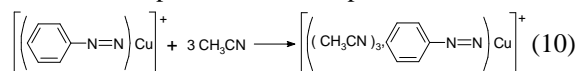


Fig. 3 Optimized 3D-structure of the crystalline $[\text{Cu}(\text{CH}_3\text{CN})_4]^+\text{BF}_4^-$ complex.

Table 1 Crystallographic data for $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ and isostructural $\text{CuClO}_4 \cdot 4\text{CH}_3\text{CN}$.

Parameter	$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$		$\text{CuClO}_4 \cdot 4\text{CH}_3\text{CN}$
	This work	Literature [43]	[47]
Space group	$Pn2_1a$	$Pn2_1a$	$Pn2_1a$
a	24.142(9) Å	23.882(4) Å	24.25(2) Å
b	20.612(7) Å	20.338(3) Å	20.75(2) Å
c	8.426(3) Å	8.329(1) Å	8.42(1) Å
$\alpha = \beta = \gamma$	90°	90°	90°
Cell volume	4193(4) Å ³	4045 Å ³	4236(9) Å ³
Z	12	12	12
Temperature	293 K	173 K	295 K
$F(000)$	2384 electrons		
Number of atoms in the cell	360		
Calculated density	1.495 g cm ⁻³	1.549 g cm ⁻³	1.539 g cm ⁻³
Absorption coefficient	22.13 cm ⁻¹		
Radiation and wavelength	Mo $K\alpha$, 0.71073 Å	Mo $K\alpha$, 0.71073 Å	Mo $K\alpha$, 0.71073 Å
Mode of refinement	$F(hkl)$		
Restrictions	$F > 4\sigma(F)$		
Weighing scheme	$1/[\sigma(F)^2 + 0.0090F_o^2]$		
Extinction formalism	Sheldrick, 0.0005(1)		
Number of atom sites	90		
Number of free parameters	597		
$2\theta_{\text{max}}$	47.00°		
$(\sin\theta/\lambda)_{\text{max}}$	0.561 Å ⁻¹		
Number of measured reflections	3537		
$R(F)$	0.0952		
$R_w(F)$	0.1049	0.0437	0.0770
Goodness of fit	1.380		
Scale factor	1.382(3)		

Because this reaction proceeds in acetonitrile, CH₃CN molecules react with azophenyl copper, to form what can be regarded as a complex compound when its coordination sphere will be completed to 4:



The formation of Cu(I) mixed complexes was observed by Parsons *et al.*, who isolated and identified the [Cu₃(*dpphp*)₂(CH₃CN)_{1.7}(CH₂Cl₂)_{0.3}]ClO₄ complex (where *dpphp* – 6-diphenylphosphino-2-hydroxypyridine) [48]. This complex is unstable and decomposes into crystalline (Cu(CH₃NC)₄BF₄) and amorphous phases, the latter being a mixture of dimeric and oligomeric nitrogenated organic compounds. The mechanism of copper dissolution *via* an intermediate stage of formation of mixed azophenyl acetonitrile Cu(I) complexes correlates well with the experimental observation of partial DAS dediazotization (70%) during the interaction with copper powder.

4. Conclusions

During copper dissolution-ionization in concentrated (≥0.05 M) acetonitrile solutions of benzenediazonium tetrafluoroborate only 70% of the initial DAS had dediazotized. The remaining DAS had reduced according to an inner sphere mechanism where the products are azophenyl radicals, which can be explained by reactions of copper with both the initial diazonium salt and intermediates. The Cu–BDFB interaction is accompanied by an intense gas (N₂) evolution and a rapid change of the initial light-yellow color of the solution to purple-red with different hues that are connected with the formation of an intermediate, which corresponds to an electronic absorption band with a maximum around 420 nm. This intermediate is a complex of Cu(I), namely [Cu–(N=N–C₆H₅)(N≡C–CH₃)₃]⁺BF₄[–], where Cu is coordinated to three solvent molecules and forms a chemical bond with the azophenyl group. The complex decomposes slowly with the formation of a crystalline phase, which was identified as [Cu(N≡C–CH₃)₄]⁺BF₄[–], and an amorphous phase, which is a mixture of oligomers containing phenyl and azophenyl fragments.

Acknowledgements

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