

## Preparative Electrochemical Reduction of Decafluorobenzil

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**Abstract**—Preparative electrochemical reduction of decafluorobenzil in DMF on a platinum electrode at the potential of the first peak afforded decafluorobenzophenone as the principal product. The reaction mixture lacked products of hydrodefluorination of the decafluorobenzil or of its reduction at the C=O group.

Electronic structure and reactivity of anion-radicals from haloaromatic compounds were recently extensively investigated [1–4]. The anion-radicals of this type attract interest to a large extent because their fragmentation furnishing aryl radicals and haloanions constitutes an elementary stage of nucleophilic substitution of the  $S_{RN}1$  type and of reductive dehalogenation.

One way to investigate the reactivity of electrochemically-generated anion-radicals is analysis of compounds arising at preparative electrolysis. We formerly studied preparative electrochemical reduction of fluorinated benzonitriles [5] in aprotic media. In extension of the research in the field of electrochemical reduction of polyfluorinated aromatic compounds in DMF we turned our attention to the study of decafluorobenzil ( $C_6F_5COCOC_6F_5$ ) that alongside C–F bonds contained additionally two potential reaction sites like C=O groups.

The electrochemical reduction of unsubstituted benzil on various electrodes in aprotic [6–12] and water media at different pH [10, 12–16] is sufficiently well documented. In aprotic media it undergoes successive one-electron reduction into anion-radical and further into dianion [11,12]. In the course of the benzil reduction in acidic and neutral water solutions a single reduction wave is observed on the polarogram, and in alkaline solutions two waves appear [10]. Philp *et al.* indicated that the second wave appeared at the potential where under similar condition benzoin was reduced [10]. The fact of existence of the second wave at the use of alkaline solutions was ascribed to acceleration in this medium of rearrangement into benzoin suffered by the endiol formed at the first wave potential [10].

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In the preparative electrochemical reduction of benzil both in aprotic and water media a reduction of a single carbonyl group was observed, and benzoin was obtained as the reduction product [7, 17]. In going to perfluorinated benzil it was presumable that alongside C=O group reduction might occur also the reduction of C–F bonds for these bonds were known to be reduced in the case of polyfluorinated aromatic compounds containing electron-withdrawing substituents giving as a result products of hydrodefluorination [5, 18].

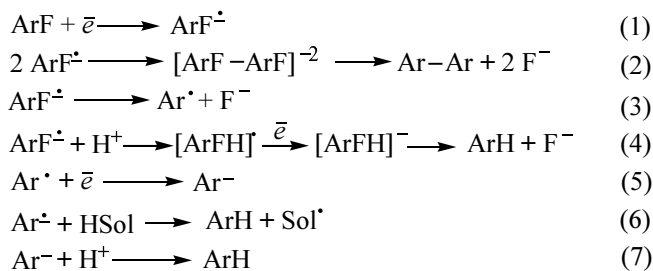
As to decafluorobenzil, the only publication concerning this compound [19] contained the reduction potential of the decafluorobenzil in acetonitrile on the mercury electrode measured with respect to the saturated calomel electrode ( $E_{1/2} -0.502$  V). Laev and Shteingarts basing on coulometric data for *p,p'*-dimethoxybenzil and benzil and on the linear dependence of  $E_{1/2}$  on  $\Sigma\sigma_X$  in the series of nonfluorinated benzils ( $X \neq NO_2$ ) concluded that the reduction of all benzil derivatives occurred with transition of one electron. The preparative electrolysis was not performed in [19].

Taking into consideration the presence in the decafluorobenzil of several probable reaction sites we investigated the process of its electrochemical reduction by preparative electrolysis in DMF on platinum electrode aiming to elucidate which among the possible pathways is realized. To determine the conditions of the preparative electrolysis we studied by cyclic voltammetry the first reduction peak of decafluorobenzil in DMF on platinum electrode. At the rate of electrode polarization  $100 \text{ mVs}^{-1}$  on the cyclic voltammogram of this compound a reduction peak  $E_p^1 -0.46$  V was observed that was

diffusion-controlled, electrochemically reversible ( $E_p^a - E_p^k$  0.06,  $E_{p/2} - E_p$  0.06 V), and corresponded to one-electron transfer\*. On the anode branch of the cyclic voltammogram a peak was clearly seen corresponding to the oxidation of the arising anion-radical of decafluorobenzil into the initial compound.

The ratio of the current in anode and cathode peaks  $I_p^a/I_p^k$  for the first reduction peak of decafluorobenzil on the cyclic voltammogram at relatively low polarization rate of electrode is less than unity ( $v$  100 mVs<sup>-1</sup>,  $I_p^a/I_p^k$  0.77) testifying to insufficient stability of the arising anion-radical that evidently suffers chemical transformations. The unstable anion-radicals forming at one-electron reduction of fluoroaromatic compounds [equation (1)] are known to undergo commonly dimerization [equation (2)], fragmentation at the C–F bond [equation (3)], or in the presence of proton sources get protonated giving radical species that further are reduced into anion which through fluoride anion elimination affords the hydrodefluorinated product [equation (4)] (Scheme 1) [20].

#### Scheme 1.



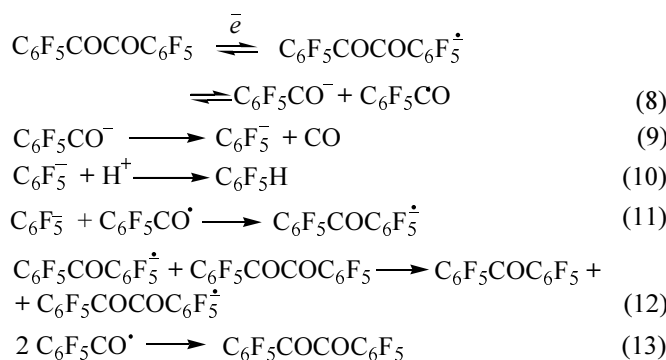
Inasmuch as at recording several cycles on the cyclic voltammogram of decafluorobenzil in the more positive potential region no additional peaks appeared that could be attributed to the reduction of dimeric reaction products [21] the expected reduction sites in preparative electrochemical reduction should be either C=O group or C–F bond.

However after the preparative electrolysis of decafluorobenzil at the potential of the first peak ( $E - 0.55$  V) the reaction mixture lacked products of decafluorobenzil hydrodefluorination or its reduction at the C=O group: The main reaction product was decafluorobenzophenone. Some pentafluorobenzene was

\* Detailed study of perfluorobenzil electrochemical reduction in DMF by cyclic voltammetry and of the structure of anion-radical formed is planned to be performed further.

also detected in the reaction mixture. This result permits a conclusion that the processes shown on Scheme 1 and also reduction at C=O group do not operate or at least are not dominant. It is presumable that the electrolysis products arise after fragmentation of the decafluorobenzil anion-radical, but the rupture occurs not at the C–F, but at C–C bond. As a result form pentafluorobenzoyl anion and a radical [equation (8)] (Scheme 2).

#### Scheme 2.



The pentafluorobenzoyl anion decomposes further into pentafluorophenyl anion and CO. The arising pentafluorophenyl anion may react with the pentafluorobenzoyl radical to yield decafluorobenzophenone anion-radical [equation (11)], or with a proton source (residual water in the solvent, solvent or supporting electrolyte [22]) to give pentafluorobenzene [equation (10)]. Inasmuch as the decafluorobenzophenone has a more negative reduction potential ( $E_{1/2}$  –1.21 V with respect to the saturated calomel electrode in THF [23]) than decafluorobenzil, the forming decafluorobenzophenone anion-radical interacting with the initial decafluorobenzil transmits the excessive electron to the latter [equation (12)]. As a result the decafluorobenzil anion-radical appears again in the reaction mixture, this time without participation of the electrode. The pentafluorobenzoyl radical besides the reaction with pentafluorophenyl anion can undergo dimerization to the initial decafluorobenzil, and the pentafluorophenyl anion can react with the initial decafluorobenzil affording addition products [24].

According to GC-MS data the reaction mixture apart from decafluorobenzophenone and pentafluorobenzene contained in small amounts compounds whose molecular mass (558 and 538) corresponded to addition of one C<sub>6</sub>F<sub>5</sub> fragment to decafluorobenzil (cf. [24]) or C<sub>6</sub>F<sub>5</sub>CO fragment to decafluorobenzophenone.

The fact of predominant reaction of the pentafluorophenyl anion with pentafluorobenzoyl radical and not with

the initial decafluorobenzil which was present in a larger amount [24] indicated that the process apparently occurred prevalingly in a "cage".

The number of electrons transmitted per substrate molecule in the course of reduction estimated from the quantity of electricity consumed amounted 0.2 in a good agreement with the suggested mechanism. The reaction mixture also contained in conformity to Scheme 2 some reaction products (in overall amount ~5 wt%) that according to the molecular mass and the mass spectral data were tentatively regarded as compounds generated by reduction of the decafluorobenzophenone at the C–F bonds (mono- and dihydrodefluorinated derivatives) and also at the C=O bond. These compounds formed apparently concurrent with reaction (12) from the anion-radical of the decafluorobenzophenone.

The concurrent elimination of CO from the pentafluorobenzoyl radical cannot be absolutely excluded, but if this process is operative, it apparently is not important.

It should be noted that the preparative electrochemical reduction of decafluorobenzil proceeds sufficiently rapidly and completely. In 1 h the control voltammograms did not contain even a trace of the reduction peak of the initial compound and an extended reduction peak appeared in the more negative potential region ( $E_p$  –1.10...–1.20 V). This peak corresponds presumably to decafluorobenzophenone reduction: This assumption is supported by the composition of the reaction mixture, and also by published value of the reduction potential of the decafluorobenzophenone ( $E_{1/2}$  –1.21 V with respect to the saturated calomel electrode in THF [23]). Another among the main reaction products, pentafluorobenzene, is reduced at notably more negative potential [ $E_p$ (C<sub>6</sub>F<sub>5</sub>H) –2.31 V] [25]. It is worth noting that on the cyclic voltammograms of decafluorobenzil no reduction peak appeared at potentials –1.1...–1.2 V showing that apparently during the measurement of voltammogram the decafluorobenzophenone had not yet enough time to form.

## EXPERIMENTAL

Cyclic voltammograms were registered on a modified electrochemical system CBA-1AM with a triangular pulse of potential scanning. The cell used was of net volume 5 ml and was connected to the system by three-electrode connection diagram. As working electrode served a stationary needle platinum electrode of area 8 mm<sup>2</sup>, as auxiliary electrode a platinum spiral was used,

and the reference electrode was the saturated calomel electrode.

In the electrochemical measurements were used solutions of initial compounds in DMF of  $2 \times 10^{-3}$  M concentration, as supporting indifferent electrolyte tetraethylammonium perchlorate was applied of 0.1 M concentration. The oxygen was removed from the cell by flushing with argon. Anhydrous DMF was obtained by two-fold vacuum distillation over phosphorus pentoxide collecting the fraction boiling at 24°C (2 mm Hg).

The preparative electrolysis was carried out with the use of potentiostat P-5848 in potentiostatic mode in a three-electrode cell. As cathode a platinum plate was used of 1 cm<sup>2</sup> area, a platinum spiral served as anode. As reference electrode was used the saturated calomel electrode. On completing the electrolysis the reaction mixture was analyzed by GC-MS method on a Hewlett-Packard G 1801 A instrument including a gas chromatograph HP 5890 of series II and mass-selective detector HP 5971, capillary column HP-5MS, 30 m × 0.25 mm × 0.25 μm, carrier gas helium, flow rate 1 ml per min, oven temperature programmed as follows: 2 min at 50°C, from 50 to 280°C at a rate 10 deg/min, 10 min at 280°C, vaporizer temperature 280°C; ion source temperature 175°C. Mass scanning was performed from 30 to 650 *m/z*.

The preparative electrolysis and cyclic voltammetry was performed using decafluorobenzil, mp. 78–79°C (according to GC-MS the content of the main substance was 99%) (publ.: mp 79–80°C [26]), as reference compounds were applied pentafluorobenzene and decafluorobenzophenone containing no less than 98% of the main compound (GC-MS data).

**Preparative electrochemical reduction of decafluorobenzil.** Into an electrochemical cell was charged 0.1 M solution of tetraethylammonium perchlorate in DMF (5 ml into cathode space and 4 ml into anode space), into the cathode space an appropriate amount of decafluorobenzil (39 mg, *C* 0.02 mol l<sup>-1</sup>) was added, and the cell was charged at *E* –0.55 V. The electrolysis was carried out at this voltage with stirring at room temperature. Due to volatile products formation the cell was flushed with argon after charging the decafluorobenzil, and electrolysis was further continued under argon atmosphere. The reaction progress was monitored by cyclic voltammograms of the reaction mixtures measured intermittently in the course of the process. After 1 h of the process on the test voltammograms the reduction peak of decafluorobenzil already disappeared, but the

electrolysis was still continued for 30 min to ensure complete reduction of the initial compound. On completing the electrolysis the reaction mixture from the cathode space was poured into 20 ml of water (pH of the solution was ~ 7), the reaction products were extracted into ethyl ether (5×7 ml), the extract was washed from DMF traces with distilled water (3×10 ml), and dried on magnesium sulfate. Then the ether was evaporated to residual solution volume ~4 ml, and the products were analyzed by GC-MS method in comparison with authentic samples. Residue after complete removal of solvent weighed 20.2 mg and contained 85.6% of decafluorobenzophenone (GC-MS data).

We failed to estimate quantitatively the pentafluorobenzene content in the reaction mixture for after workup the overall concentration of products in solution did not exceed 0.1 wt%, and at attempted concentrating of solution the volatile pentafluorobenzene was eliminated with the solvent. However even in this situation its trace amounts were detected by GC-MS method.

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