

Electrochemical Reduction of Decafluorobenzil in DMF on a Platinum Electrode

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Abstract—The mechanism of electrochemical reduction of decafluorobenzil on a platinum electrode in DMF was investigated by cyclic voltammetry. The first reduction peak corresponded to a reversible single-electron transfer leading to the formation of a relatively stable anion-radical whose ESR spectrum was registered and characterized. The second peak corresponded to the reduction of the anion-radical into an unstable dianion that quickly reacted with initial decafluorobenzil, and the arising species (or its transformation product) at the given potential underwent further reduction. The effect of fluorine on the potentials and on the mechanism of the electrochemical reduction of decafluorobenzil was considered.

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In extension of investigation of electrochemical reduction of polyfluorinated aromatic compounds in aprotic media we studied the process by an example of a representative of α -diketones decafluorobenzil ($C_6F_5COCOC_6F_5$), that alongside the C–F bonds contained two carbonyl groups. We formerly investigated the preparative electrochemical reduction of decafluorobenzil [1]. This study concerns the investigation of the mechanism of electrochemical reduction of decafluorobenzil by cyclic voltammetry (CVA) and ESR and the revealing the effect produced by the replacement of the hydrogen atoms in benzil by fluorine on the mechanism and potentials of the electrochemical reduction.

The electrochemical reduction of unsubstituted benzil on various electrodes in aprotic [2–8] and water media in a wide range of pH [6, 8–12] was subjected to sufficiently detailed study. It was established that in aprotic environment on a mercury electrode the benzil underwent successive single-electron reduction into anion-radical and further into dianion [7, 8]. The investigation carried out with a glass-carbon electrode in DMF showed that the benzil anion-radical was stable whereas the reversibility of the second reduction peak was observed only at multiple scanning of potential and in the presence of proton source in the solution [8].

The electrochemical reduction of decafluorobenzil was mentioned in a single publication [13], where alongside the data on the other p,p' -disubstituted benzils the reduction potential of decafluorobenzil on a mercury electrode was reported measured in acetonitrile with respect to the saturated calomel electrode ($E_{1/2} - 0.502$ V). From the coulometric data for p,p' -di-methoxybenzil and benzil and the linear dependence of $E_{1/2}$ on $\Sigma\sigma_X$ in the series of nonfluorinated benzils ($X \neq NO_2$) a conclusion was made that a single-electron transfer occurred in reduction of all benzil derivatives. The detailed mechanism of reduction of benzil and its derivatives was not discussed in [13].

In this study we investigated the electrochemical reduction of decafluorobenzil in DM on a platinum electrode by CVA method.

On the cathode branch of the cyclic voltammogram of decafluorobenzil two reduction peaks were observed [1K ($E_p^{1K} - 0.46$ V), 2K ($E_p^{2K} - 1.76$ V)], on the anode branch appeared two oxidation peaks (1A and 1a) (Fig. 1). The first reduction peak 1K is reversible ($E_p^{1A} - E_p^{1K} = 0.06$ V), it is diffusion-controlled and corresponds to the transfer of a single electron. The arising anion-radical, although relatively stable, undergoes further transformations (at the velocity of the electrode polarization less than 500 mV/s $I_p^{1A}/I_p^{1K} < 1$). The one-electron

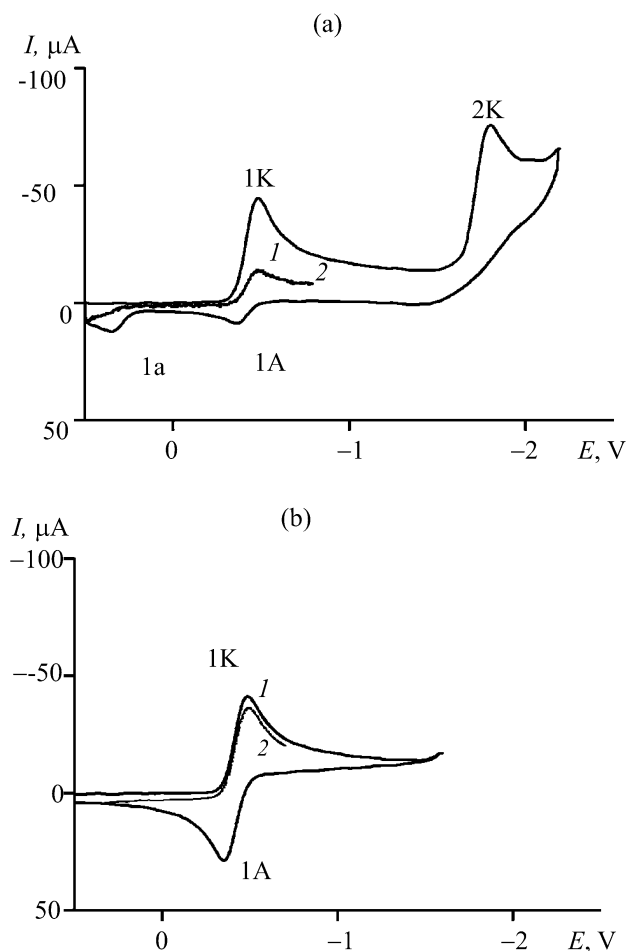


Fig. 1. Cyclic voltammogram of decafluorobenzil reduction in DMF–0.1M solution of Et_4NClO_4 (v 100 mV/s): reverse point of potential –2.2 (a), –1.6 V (b) (1 and 2 are numbers of voltammogram cycles).

transfer at the potential of the first peak was confirmed by registering the ESR spectrum of the anion-radical obtained by electrochemical generation at the potential of the first peak (Fig. 2). The character of superfine interactions in the ESR spectrum [$a_{p-F}(2\ ^{19}\text{F})$ 0.84, $a_{o-F}(4\ ^{19}\text{F})$ 0.47, $a_{m-F}(4\ ^{19}\text{F})$ 0.38 Gauss] indicates the spectral equivalence of the two pentafluorophenyl rings in the anion-radical of decafluorobenzil and the occurrence of free rotation of the molecular fragments around the C–C bonds. The very small values of the constants of superfine interactions on the ^{19}F nuclei of the pentafluorophenyl rings are due the distribution of the spin density mainly on the carbonyl groups of the molecule. The half-life of ($\tau_{1/2}$) of the anion-radical of decafluorobenzil estimated by ESR method is 57 s. We formerly demonstrated that the principal mechanism of the anion-radical decomposition was its fragmentation

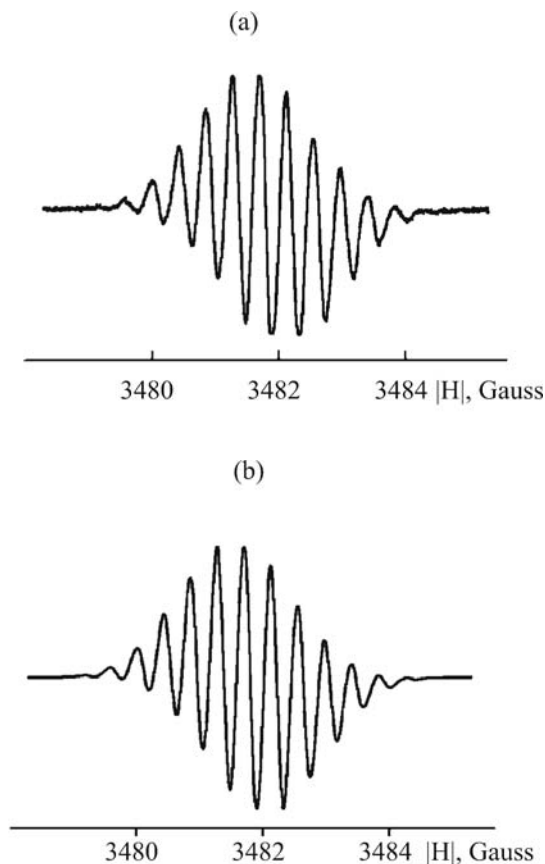


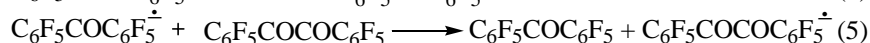
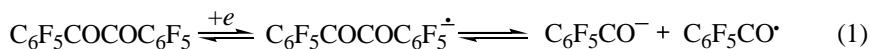
Fig. 2. ESR spectrum of decafluorobenzil anion-radical (a) and its mathematical simulation (b). Constants of superfine interaction a_{i-F} ($2\ ^{19}\text{F}$) 0.84, a_{o-F} ($4\ ^{19}\text{F}$) 0.47, a_{m-F} ($4\ ^{19}\text{F}$) 0.38 Gauss, basic linewidth Γ_0 0.11 Gauss, correlation factor r 0.999.

at the C–C bond with the formation of pentafluorobenzoyl anion and radical [1]. The fragmentation constant calculated from the ratio of the anode and cathode current I_p^{1A}/I_p^{1K} was according to [14] k_{fr} 1.1×10^{-2} s $^{-1}$ in good agreement with the value we obtained from the ESR measurements (k_{fr} 1.2×10^{-2} s $^{-1}$).

We showed in [1] that at the preparative electrochemical reduction of decafluorobenzil at the potential of the first peak the main reaction product was decafluorobenzophenone, and the most probable mechanism of its formation was suggested (Scheme 1).

However on the cyclic voltammogram of decafluorobenzil at the velocity of electrode polarization v 100 mV/s we did not find any additional peak that could be assigned to decafluorobenzophenone reduction. In keeping with the estimated fragmentation constant of the decafluorobenzil anion-radical it is presumable that at the used electrode polarization velocity 100 mV/s in the

Scheme 1.



time range of CVA the decafluorobenzophenone does not form in notable amount in the course of registering the first cycle. The increase in the registering time of the voltammogram by diminishing the electrode polarization velocity to 20 mV/s did not result in appearance of the peak of decafluorobenzophenone. The reduction peak of decafluorobenzophenone at -1.11 V we succeeded to observe only by registering several cyclic voltammogram in succession or by performing microelectrolysis at the potential of the first peak (maintaining the potential at $E = -0.6$ V for 3–4 min with subsequent registering of the cyclic voltammogram); however the current of this peak is very small (~ 1 μA) indicating the negligible amount of the product. This fact can be understood from Scheme 1 on condition of the short lifetime of the decafluorobenzophenone anion-radical. According to equation (5) the decafluorobenzophenone formed from the corresponding anion-radical by a fast electron transfer from these anion-radical to the initial decafluorobenzil. In the CVA experiment the decafluorobenzil concentration is 10 times less that in our experiments of preparative electrolysis, therefore at the low decafluorobenzil concentration ($C = 2 \times 10^{-3}$ mol l^{-1})

the unstable decafluorobenzophenone anion-radical perishes before it meets the molecule of the initial compound. In the study of decafluorobenzophenone reduction under identical experimental conditions we actually showed the instability of its anion-radical. The first reduction peak of decafluorobenzophenone is irreversible up till the electrode polarization velocity 100 V/s, at $v = 100$ mV/s the potential of reduction peak equals $E_p^{1K} = -1.11$ V. Consequently, at the use of low concentrations of decafluorobenzil (under conditions of CVA registering) no decafluorobenzophenone formed at the potential of the first reduction peak, and the reaction occurred further by another mechanism than that of preparative electrolysis.

Peak 2K on the voltammogram of decafluorobenzil corresponds to further reduction of decafluorobenzil anion-radical to dianion since the decafluorobenzil anion-radical is sufficiently stable in the time scale of CVA registering (Fig. 1b).

The irreversibility of 2K peak up till electrode polarization velocity 100 V/s indicated the low stability of the species formed. This fact and also the relatively high current of this peak ($I_p^{2K} > I_p^{1K}$, 59 and 47 μA)

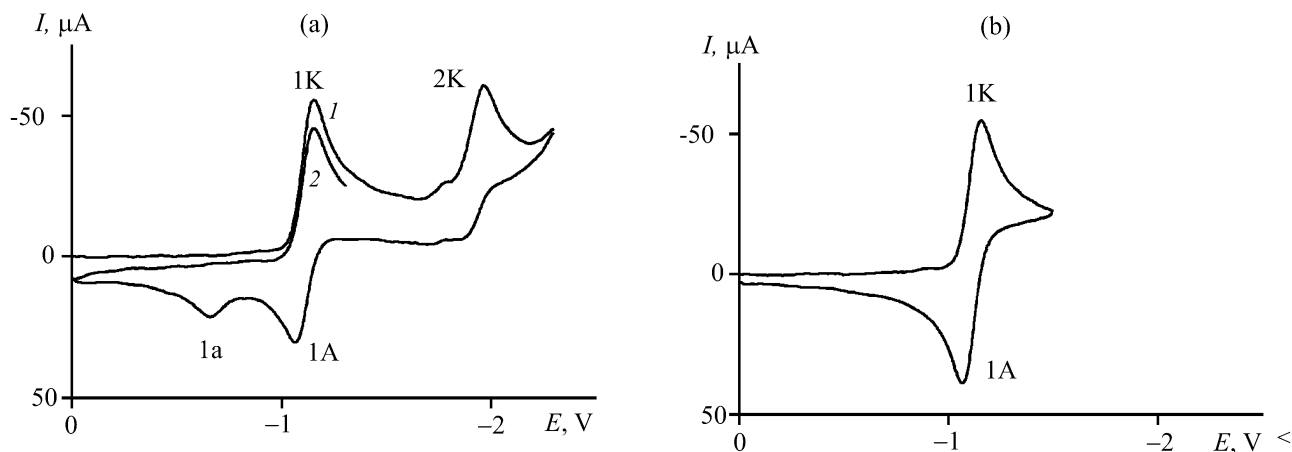


Fig. 3. Cyclic voltammogram of benzil reduction in DMF-0.1 M solution of Et_4NClO_4 ($v = 100$ mV/s) on a platinum electrode: reverse point of potential -2.40 (a), -1.5 V (b) (1 and 2 are numbers of voltammogram cycles; $E_p^{1K} = -1.13$, $E_p^{2K} = -1.93$ V).

respectively) evidence that the arising dianion is unstable and suffers fast chemical transformation into an electrochemically active species which is reduced further at this potential. The instability of the decafluorobenzil dianion may be caused both by its high basicity and by the fast reaction with proton sources (residual water in the solvent or solvent itself), or by its nucleophilic characteristics revealed, for instance, in the reaction with the initial decafluorobenzil.

In order to establish whether the decafluorobenzil anions perish due to its basic properties we carried out experiments with water addition to the electrochemical cell before registering the cyclic voltammograms. The addition into the cell fivefold and tenfold molar excess of water with respect to the substrate did not affect the appearance of the cyclic voltammogram (the reduction potentials values and the corresponding currents remain unchanged). Consequently the formation of an electrochemically active species at the second reduction peak potential is not caused by protonation with water traces in the solvent or by the solvent itself; otherwise the current of peak 2K should grow.

At scanning of the potential up to -2.2 V on the second and subsequent voltammogram cycles a very strong decrease in the current of the first reduction peak 1K was observed (first cycle $I_p^{1K} -48 \mu\text{A}$, second cycle $I_p^{1K} -10 \mu\text{A}$); this was not observed when the scanning of potential was performed before the beginning of the second reduction peak (first cycle $I_p^{1K} -48 \mu\text{A}$, second cycle $I_p^{1K} -44 \mu\text{A}$) (Fig. 1a, b).

This fact suggests a strong reduction of the initial decafluorobenzil concentration near electrode at the polarization of the main electrode in the region of the second peak potential. Consequently, the considerable decrease in the concentration of the initial decafluorobenzil that was observed near the electrode after formation there of decafluorobenzil dianion originated from the fast reaction of the forming decafluorobenzil dianion with the initial decafluorobenzil. The arising species (or its transformation product) suffered further reduction at these potential thus increasing the current of peak 2K compared with the current of peak 1K.

At the reverse scanning of the potential from the region of the second peak potentials on the anode branch of the cyclic voltammogram of decafluorobenzil beside the peak of oxidation of decafluorobenzil anion-radical to the initial compound (peak 1A) a definite anode peak 1a was observed at $+0.33$ V (Fig. 1a) that was absent at the scanning of potential only in the region of the first

peak (Fig. 1b) and that consequently corresponded to the oxidation of the product of further chemical and electrochemical transformations of the decafluorobenzil dianion. The microelectrolysis at the potential of the second reduction peak resulted in considerable decrease in the anode peak 1A in conformity to the diminished amount of the initial compound near the electrode.

Thus the results obtained at several cycles of potential scanning and on adding various water concentrations as proton source suggest that peak 2K originates from the reduction of decafluorobenzil anion-radical to dianion which quickly reacts with the initial decafluorobenzil. The species arising in that way or the product of its transformation undergoes further reduction at the second peak potential. Consequently, the electrochemical reduction of decafluorobenzil is a process EEC_nE ($n \geq 1$).

To reveal the effect of hydrogen replacement in benzil by fluorine on the mechanism and potentials of the electrochemical reduction we also investigated the electrochemical behavior of unsubstituted benzil under identical experimental conditions. The cyclic voltammograms of benzil reduction are presented on Fig. 3.

The comparison of reduction potentials of benzil and decafluorobenzil (Fig. 1a and 3a) shows that the effect of 10 fluorine atoms in perfluorobenzil on the first reduction peak potential is fairly essential: on replacement of hydrogen by fluorine the first peak potential shifts to the anode region approximately by 0.67 V. This replacement affects the second peak potential considerably less, the shift of the potential to the anode region is but 0.17 V. Note that decafluorobenzil possesses high affinity to electron: It is reduced at about the same potential as *p*-dinitrobenzene [15]. As to the mechanism of the electrochemical process, in both cases the arising anion-radicals are sufficiently stable (Fig. 1b and 3b). The pathways of these anion-radicals transformations on the preparative electrolysis scale are different: Whereas the benzil anion radical gives finally benzoin [3, 16], the transformations of decafluorobenzil anion-radical result in decafluorobenzophenone formation [1]. At the potential of the second peak benzil provides relatively stable dianion (at $v \geq 200$ mV/s the reversibility of peak 2K is clearly seen). The dianion of decafluorobenzil is unstable, peak 2K of decafluorobenzil is irreversible even at the high velocity of the electrode polarization (v 100 V/s). The relatively stable benzil dianion does not react with the initial compound according to CVA data (Fig. 3a), whereas this transformation is the main one for the polyfluorinated derivative. For both com-

pounds the anode peak 1a observed at the reverse scanning of potential is due to the products formed at the potential of the peak 2K (Fig. 1a, b, 3a, b).

EXPERIMENTAL

Cyclic voltammograms were registered on a modified electrochemical system SVA-1BM with a triangular pulse of potential scanning. We used a cell of working volume 5 ml connected to a system by three-electrode scheme and equipped with a salt bridge with a solution of supporting electrolyte in DMF for connecting the working and reference electrodes. The working electrode was stationary spherical platinum electrode of area 8 mm², the auxiliary electrode was a platinum spiral. As reference electrode the saturated aqueous calomel electrode was used. The electrochemical measurements were performed on solutions of the initial compounds in DMF (2×10^{-3} mol l⁻¹), we used as supporting electrolyte tetraethylammonium perchlorate of concentration 0.1 mol l⁻¹. The oxygen was removed from solvents by flushing the cell with argon. Anhydrous DMF was obtained by double distillation in a vacuum over phosphorus pentoxide collecting the fraction of bp 24°C (2 mm Hg).

In the study were used decafluorobenzil, mp 78–79°C (according to GC-MS data the content of the main compound was 98.9%) (mp 79–80°C [17]), benzil and decafluorobenzophenone containing no less than 98% of the main substance (by GC-MS data).

The ESR spectrum of decafluorobenzil anion-radical was recorded on a spectrometer Bruker ESP-300, equipped with double resonator (power of microwave radiation 256 mW, modulation frequency 100 kHz modulation amplitude 0.05 Gauss). The reduction of decafluorobenzil combined with ESR spectrometric measurements was done under air-free conditions at 298 K at the potential of the first reduction peak in a three-electrode cell with a platinum electrode. The

working electrode of the cell was placed into the resonator of ESR spectrometer. The numerical simulation of the ESR spectra was carried out using WINSIM 32 program with an algorithm of multi-parameter optimization LMB1.

REFERENCES

1. Vasil'eva, N.V. and Starichenko, V.F., *Zh. Org. Khim.*, 2004, vol. 40, p. 1180.
2. Kargin, Yu.M. and Kondranina, V.Z., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, p. 565.
3. Arthur, P., Rulison, D.S., and Berlin, K.D., *Anal. Chem.*, 1968, vol. 40, p. 1389.
4. Buchta, R.C. and Evans, D.H., *Anal. Chem.*, 1968, vol. 40, p. 2181.
5. Talant, D.R. and Evans, D.H., *Anal. Chem.*, 1969, vol. 41, p. 835.
6. Philp, R.H., Flurry, R.L., and Day, R.A., *J. Electrochem. Soc.*, 1964, vol. 111, p. 328.
7. Philp, R.H., Layloff, T., and Adams, R.N., *J. Electrochem. Soc.*, 1964, vol. 111, p. 1189.
8. Chandrasekaran, M., Noel, M., and Krishnan, V., *J. Chem. Soc., Perkin Trans. 2*, 1992, p. 979.
9. Stapelfeldt, H.E. and Perone, S.P., *Anal. Chem.*, 1968, vol. 40, p. 815.
10. Stapelfeldt, H.E. and Perone, S.P., *Anal. Chem.*, 1969, vol. 41, p. 623.
11. Vincenz-Chodkowska, A., and Grabowski, Z.R., *Electrochim. Acta*, 1964, vol. 9, p. 789.
12. Meunier-Prest, R., Laviron, E., Gaspard, C., and Raveau, S., *Electrochim. Acta*, 2001, vol. 46, p. 1847.
13. Clenan, E.L., Speth, D.R., and Barlett, P.D., *J. Org. Chem.*, 1983, vol. 48, p. 1246.
14. Nicholson, R.S. and Shain, I., *Anal. Chem.*, 1964, vol. 36, p. 706.
15. Allendoerfer, R.D. and Rieger, P.H., *J. Am. Chem. Soc.*, 1966, vol. 88, p. 3711.
16. Pasternak, H., *Helv. Chim. Acta*, 1948, vol. 31, p. 753.
17. Chambers, R.D., Clark, M., and Spring, D., J., *J. Chem. Soc., Perkin Trans. 1*, 1972, p. 2464.