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One-Electron Transfer in Electrochemical Oxidation of Calix[4]resorcinolarenes and Their Aminomethylated Derivatives

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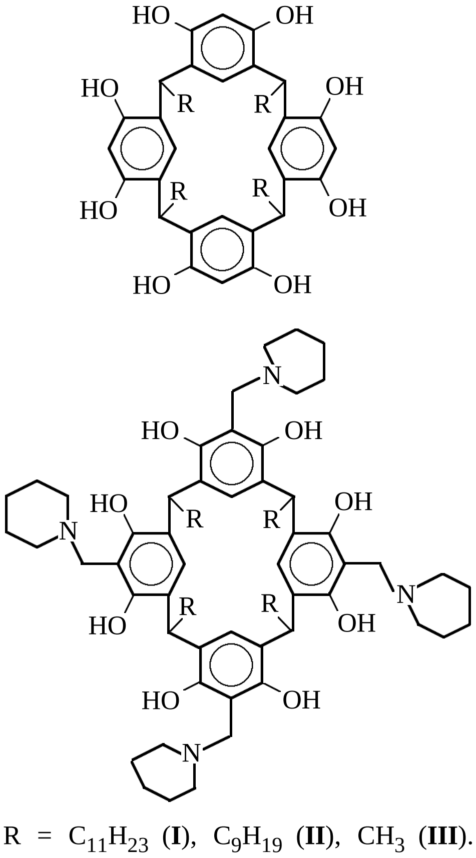
Abstract—Calix[4]resorcinolarenes in the presence of amine and aminomethylated calix[5]resorcinolarenes in DMF undergo similar multistage electrochemical oxidation. The first stage proceeds at low potentials and involves reversible one-electron transfer with formation of stable phenoxy radicals.

Electrochemical oxidation of simple phenols has been studied in sufficient detail (see, e.g., [1]), and the effect of the structure and solvent on the reaction mechanism and direction was elucidated. The reaction proceeds via formation of phenoxy radical and phenoxonium ion. In acidic and alkaline solutions, products of transformation of phenoxonium ion and of phenoxy radical, respectively, are formed. Phenoxy radicals are stable in the case of 2,4,6-trisubstituted sterically hindered phenols and are detected under common conditions by ESR spectroscopy and cyclic voltammetry [2]. The easiness of phenol oxidation and the stability of the resulting radical are the most important characteristics determining the antioxidant power of sterically hindered phenols. Phenoxy radicals can behave as both electron donors and electron acceptors. Metal complexes with macrocylcic ligands containing sterically hindered phenols are considered as a basis for development of homogeneous redox-catalytic systems of a new type with a controllable catalytic effect [3].

In this context, of certain interest are macrocyclic phenols, calixarenes; however, their electrochemical oxidation was not studied. In this work, using cyclic voltammetry and electrolysis in combination with ESR, we studied electrochemical oxidation of calix[4]resorcinolarene **I** and its aminomethylated derivatives **II** and **III** on a carbon glass electrode in the system DMF/Et_4NBF_4 (c 0.1 M).



R = $C_{11}H_{23}$ (**I**), C_9H_{19} (**II**), CH_3 (**III**).

The cyclic voltammograms of **I** contain a single irreversible oxidation peak (Fig. 1). The peak current corresponds to transfer of two electrons per molecule. A similar pattern is observed in oxidation of simple phenols, in particular, resorcinol (Fig. 2). In this respect, electrochemical oxidation of **I** is similar to oxidation of simple phenols and probably involves formation of the phenoxonium ion. The difference is that the macrocycle significantly facilitates oxidation of **I** as compared to resorcinol (ΔE_p 0.26 V).

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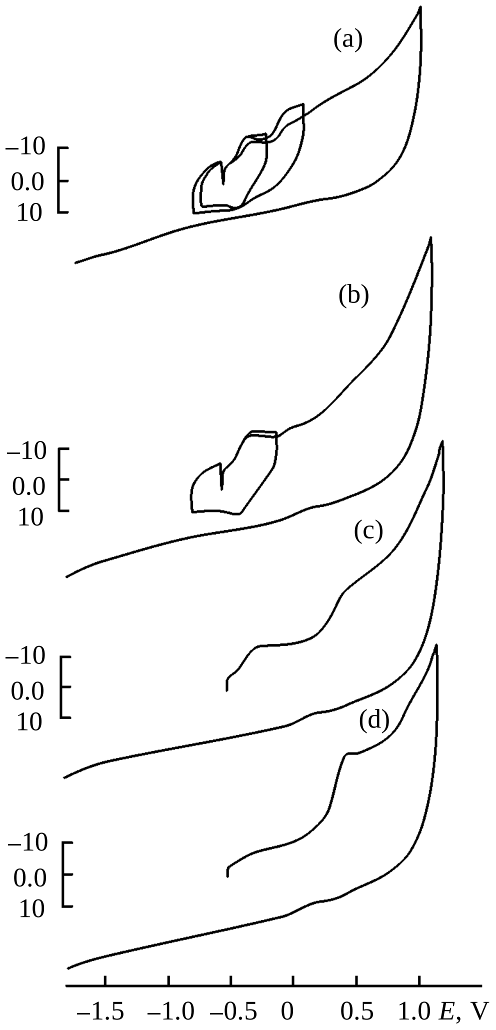

Fig. 1. Cyclic voltammograms of a 10^{-3} M solution of calix[4]resorcinolarene **I** in DMF/Et_4NBF_4 (*c* 0.1 M) on a carbon glass electrode in the presence of piperidine. Piperidine concentration, M: (a) 4×10^{-3}, (b) 2×10^{-3}, (c) 1×10^{-3}, and (d) 0. Potential sweeping rate *v* 100 mV s^{-1}.

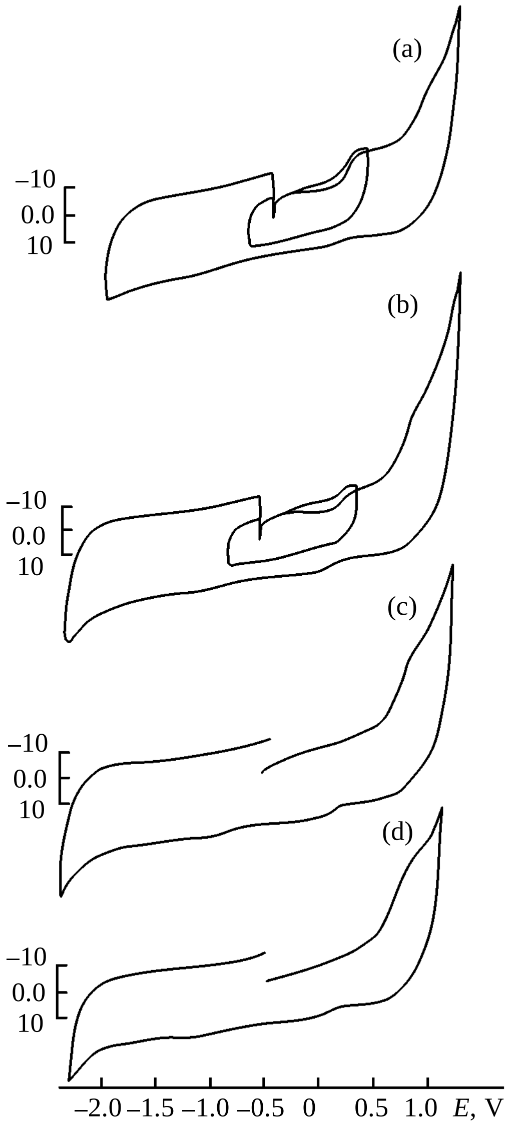

Fig. 2. Cyclic voltammograms of a 10^{-3} M solution of resorcinol in DMF/Et_4NBF_4 (*c* 0.1 M) on a carbon glass electrode in the presence of piperidine. Piperidine concentration, M: (a) 4×10^{-3}, (b) 2×10^{-3}, (c) 1×10^{-3}, and (d) 0. Potential sweeping rate *v* 100 mV s^{-1}.

Introduction of aminomethyl group (compounds **II** and **III**) significantly affects the redox properties of **I**. The cyclic voltammograms of aminomethylated derivatives **II** and **III** contain three (**III**) or four (**II**) oxidation peaks (Fig. 3). The characteristics of the first three peaks are independent of the length of the hydrocarbon radical R. Both these peaks are shifted toward lower potentials relative to the oxidation peak of I. The strongest first peak with the limiting current corresponding to one-electron transfer is reversible ($\Delta E_p^{a,c}$ 60 mV, i_p^c/i_p^a 1.0), and the subsequent less intense peaks are irreversible. The reversible one-electron oxidation is also observed in 2-propanol containing 0.1 M Bu_4NBr as supporting electrolyte. Considerable facilitation of the electron transfer as compared to **I** ($\Delta E_p^{\mathbf{I,II}} = \Delta E_p^{\mathbf{I,III}} = 0.56$ V), in combination with the reversibility and one-electron level of the limiting current, unambiguously shows that the first peak corresponds to oxidation of phenolate ions with formation of stable phenoxy radicals. Radicals of the phenoxy type, stable in DMF and *i*-PrOH, were detected by ESR in the course of electrolysis at potentials of the first peak, performed directly in the ESR spectrometer cavity.

Characteristics of oxidation waves for 10^{-3} M solutions of calix[4]resorcinolarenes **I**–**III**, resorcinol, and 2-(diethylaminomethyl)phenol in DMF/Et_4NBF_4 (*c* 0.1 M) on a carbon glass electrode

$c_{\text{piperidine}} \times 10^3$, M	E_p^{ox} [a], V	$i_p^{\text{ox}} \times 10^6$, A	n [b]	$\Delta E_p^{\text{a,c}}$ [c], mV
Compound **I**				
–	0.46	25	2.0	d
1	–0.25	7	0.6	d
	0.47			d
2	–0.28	10	0.8	120
	0.05			d
	0.47			d
4	–0.31	7	0.6	70
	0.0			d
	0.38			d
4 [e]	–0.53	14	1.1	70
	–0.10			d
	0.35			d
Compound **II**				
–	–0.10	14	1.1	60
	0.14			d
	0.35			d
	0.60			d
Compound **III**				
–	–0.10	12	1.0	70
	0.15			d
	0.31			d
Resorcinol				
–	0.72	28	2.0	d
1	0.72	26	1.9	d
2	0.25	7	0.5	d
	0.83			d
4	0.28	14	1.0	d
	0.85			d
2-(Diethylaminomethyl)phenol				
–	0.72			d

[a] The potentials are given relative to Ag/$AgNO_3$ (*c* 0.01 m) in MeCN. [b] The number of transferred electrons was estimated by comparison with the one-electron oxidation peak of 2,4,6-tri(*tert*-butyl)phenol. [c] The difference between the oxidation potential E_p^{ox} and reduction potential of the oxidation product. [d] Irreversible oxidation peak. [e] c_{Et_4NOH} 2×10^{-2} M.

It is known [4] that aminomethylated calix[4]resorcinolarenes in polar media can exist in equilibrium between the neutral and zwitter-ionic forms. Apparently, specifically the zwitter-ionic form is oxidized in DMF and *i*-PrOH at potentials of the first peak. The one-electron level of the limiting current means that aminomethylated calix[4]resorcinolarenes **II** and **III** are completely oxidized in the zwitter-ionic form. Though the equilibrium content of this form may be low, the one-electron level can be reached owing to fast shift of the equilibrium in the course of oxidation. The subsequent waves are apparently due to further oxidation of the resulting radical.

In polar media, the presence of the zwitter-ionic form is presumed also for simple aminomethylated phenols [4]. However, the high oxidation potential of 2-(diethylaminomethyl)phenol, coinciding with the oxidation potential of resorcinol (see table), suggests that in DMF only the neutral form is oxidized, with the content of the zwitter-ionic form being insignificant. These results descriptively show that the resorcinol macroring and the amino groups act in the same direction, shifting the equilibrium toward the zwitter-ionic form and thus considerably facilitating the one-electron transfer.

To reveal the role of rigid fixation of the amino group in the molecule and the effect of the macroring, we studied electrochemical oxidation of **I** and resorcinol in the presence of various concentrations of piperidine. We found that addition of amine strongly affects the anodic behavior of calix[4]resorcinolarene **I**. Even

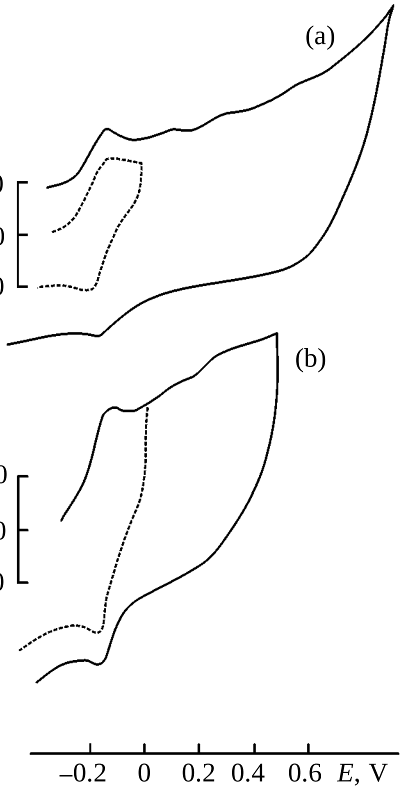

Fig. 3. Cyclic voltammograms of 10^{-3} M solutions of aminomethylated calix[4]resorcinolarenes (a) **II** and (b) **III** in DMF/Et_4NBF_4 (*c* 0.1 M) on a carbon glass electrode. Potential sweeping rate *v* 100 mV s^{-1}.

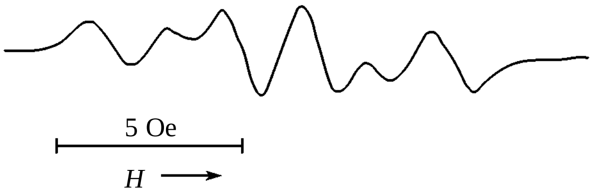

Fig. 4. ESR spectrum of phenoxy radical generated by electrochemical oxidation of a 10^{-3} M solution of calix[4]resorcinolarene **I** in DMF/Et_4NBF_4 (*c* 0.1 M) in the presence of piperidine (*c* 4×10^{-3} M) on a carbon glass electrode at +0.1 V.

at equimolar (*c* 10^{-3} M) concentration of piperidine an additional peak of oxidation of phenolate ion to phenoxy radical appears at –0.25 V. The peak current corresponds to transfer of 0.64 per molecule, i.e., more than a half of **I** delivered by diffusion to the electrode surface is oxidized in the form of the phenolate ion. At doubling the amine concentration, the quasireversible ($\Delta E_p^{a,c}$ 120 mV) first peak increases (*n* 0.8) and shifts toward more negative potentials, and an additional peak appears at +0.05 V. The oxidation peak of the neutral form is still observed, though with a considerably decreased intensity (Fig. 1). At the ratio of **I** to piperidine of 1 : 4, corresponding to the content of amino groups in aminomethylated calix[4]-resorcinolarenes, the cyclic voltammogram becomes similar to those of aminomethylated calix[4]resorcinolarenes: Three oxidation peaks are registered, with the first peak being reversible. In the case of resorcinol, addition of piperidine also results in appearance of an additional wave at low potentials, with the wave height depending on the piperidine concentration (Fig. 2; see table). However, in contrast to **I**, the wave is irreversible and is observed at more positive potentials. Hence, calix[4]resorcinolarene **I** behaves similarly to substituted resorcinol, and the effect of the macrocycle consists in facilitation of the one-electron transfer and stabilization of the resulting oxidation product.

Electrochemical oxidation of solutions of **I** in the presence of piperidine at potentials of the first peak directly in the cavity of an ESR spectrometer, similar to the case of **II** and **III**, results in appearance of an ESR signal from stable radicals of the phenoxy type (Fig. 4). The signals of all the three radicals are broadened owing to dynamic processes such as conformational equilibria of **I**–**III** in solution and possibly intramolecular electron transfer between resorcinol fragments. The spectrum of the phenoxy radical generated by oxidation of **I** is the simplest; it is a triplet of doublets. By analogy with the resorcinol radical [5], it can be interpreted as the radical of substituted resorcinol with splittings from two equivalent methine protons (a_{2H} 3.6 Oe) and from the 5-H atom of the benzene ring (a_H 2 Oe).

Our results show that the functions of the amino group fixed in a molecule of aminomethylated calix[4]resorcinolarene and of free amine in electrochemical oxidation of calix[4]resorcinolarenes are essentially similar. They act as proton acceptors, and the NH^+ protonated form is the counterion relative to the phenolate ion. A certain difference in the properties of these two systems consists in the fact that at the amine concentration of 4×10^{-3} M a part of **I** precipitates. As a result, the limiting current decreases (see table). On introduction of 2×10^{-2} M Et_4NOH, the precipitate dissolves, and the first peak shifts toward more negative potentials.

Figure 5 shows the ^1H NMR spectra of **I** in the absence and in the presence of a fourfold amount of piperidine. The spectra contain well-defined signals of aromatic ring protons at 7.5 and 6.3 ppm, a triplet of the methine proton at 4.3 ppm, and signals of the undecyl groups at 0.5–1.5 ppm. The signal broadening on addition of piperidine is due to exchange in a complex of I with piperidine. Also, the signals shift upfield by 0.2 ppm (Fig. 5b), which is typical of formation of such complexes [6]. The difference between the redox properties of aminomethylated derivatives **II** and **III** and those of calix[4]resorcinolarene **I** in the presence of a fourfold amount of piperidine is that compounds **II** and **III** are oxidized more difficultly (ΔE_p 210 mV). This means that the phenoxy radicals generated from these compounds are stronger oxidants than those generated from **I**. In outer-sphere electron transfer in oxidation of organic substrates with radicals of aminomethylated derivatives **II** and **III**, at equal other conditions, the rate constant is almost two orders of magnitude higher as compared to **I**.

The redox potentials of ion pairs depend on the nature of the counterion [7]. The smaller the size of the counterion and the distance between the ions, the stronger its effect. Apparently, in molecules of **II** and **III** rigid fixation of the amino group makes the contact in the ion pair in the zwitter ion closer than in the ion pair formed by phenolate ion and free piperidinium cation. This fact furnishes an opportunity of finely controlling the redox properties of calix[4]resorcinolarenes by varying the nature of the amino group in the aminomethylated derivatives and of amine in a mixture with **I** and also by varying the length of the hydrocarbon bridge between the amino group and macrocycle in aminomethylated calixarenes. Furthermore, the redox properties can also be dependent on

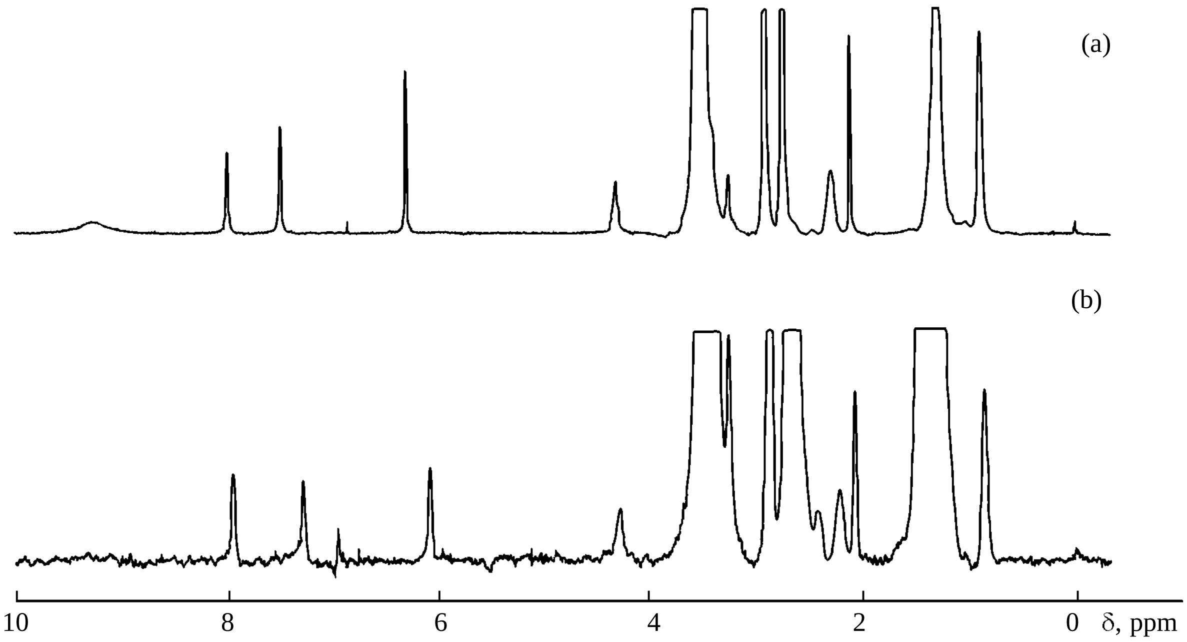

Fig. 5. ^{1}H NMR spectrum of calix[4]resorcinolarene **I** (a) in the absence and (b) in the presence of a fourfold amount of piperidine.

the concentration of calix[4]resorcinolarenes, because, as shown by measurements of the conductivity of DMF solutions, at concentrations above 10^{-3} M compound **I** tends to aggregate. Additional factors affecting the oxidation potentials are the base concentration and the nature of the solvent.

To conclude, electrochemical oxidation of calix[4]resorcinolarenes in the presence of the amino group fixed in the molecule or of a free amine occurs very readily at potentials close to the oxidation potentials of known antioxidants [8]. The process consists in reversible one-electron transfer with formation of a stable phenoxy radical. These data allow calix[4]resorcinolarenes in combination with amines to be considered as potential antioxidants and radical scavengers. On the other hand, electrochemical behavior of the studied calix[4]resorcinolarenes meets the requirements imposed on organic electron-transfer agents, and these compounds proper and/or their complexes with metals (Cu, Co, Fe) can find use as catalysts in oxidation of various organic substrates. The possibility of realization of a catalytic cycle is also suggested by the previously discovered intramolecular electron transfer in Cu(II) complexes of aminomethylated calix[4]resorcinolarenes [9].

EXPERIMENTAL

The ^{1}H NMR spectra were taken at 321 K on a Bruker spectrometer (400 MHz) in DMF-d_7 under the following conditions: *NS* 1000, *RD* 1 s, *PW* 10°.

Cyclic voltammograms were measured at 298 K with a PI-50-1 potentiostat and an N-307/2 two-coordinate recorder. The potential sweeping rate was 100 mV s^{-1}. The working electrode was a carbon glass disk electrode 2 mm in diameter, pressed in fluoroplastic. Before each measurement the electrode was mechanically polished. The reference electrode was Ag/$AgNO_3$ (c 0.01 M) in MeCN, with a potential of +0.3 V vs. saturated calomel electrode. Dissolved oxygen was removed by an argon or nitrogen flow.

Experiments on electrolysis in combination with ESR were performed at 298 K on a unit consisting of an SE/X-2544 ESR spectrometer, a potentiostat, and an electrochemical cell, allowing the electrochemical process to be performed directly in the cavity of the ESR spectrometer. The working electrode was a platinum wire, and the reference electrode, a silver wire. The solutions were deaerated by three freeze–pump–thaw cycles.

Electrochemical oxidation of calix[4]resorcinolarenes **I**–**III** was performed in DMF and 2-propanol purified by standard procedures. Compound **I** was prepared according to [10], and compounds **II** and **III**, according to [11]. Their physicochemical properties are given in [4]. As supporting electrolyte we used 0.1 M solutions of Et_4NBF_4 and Bu_4NBr purified by recrystallization from acetonitrile.

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