The dimerization of radical anions of aromatic carboxylic acids competing with the self-protonation reaction

T. Ya. Rubinskaya, * A. S. Mendkovich, N. K. Lisitsina, I. P. Yakovlev, and V. P. Gultyai

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

Quantum-chemical calculations (CNDO/2) of the theoretical relationship between the rate constants for the dimerization and self-protonation of radical anions show that dimer formation in the one-electron electroreduction of aromatic carboxylic acids (benzoic (1), 1-naphthoic (2), and 9-anthroic (3)) is most probable for 1. It is established that during the constant potential electrolysis (CPE) of 1 a mixture of "head-to-tail" dimers is formed in the presence of 0.1 M Bu₄NCIO₄ (DMF). Their ratio depends on the amount of electricity passed through the solution. The CPE of 2 in the presence of 20 % H₂O affords 1,4-dihydro-1-naphthoic acid in up to 70 % yield. The high yield (~70 %) of 9,10-dihydro-9-anthroic acid during the CPE of 3 can be accounted for by the decomposition of the dimeric product followed by protonation of the anionic species.

Key words: dimerization, self-protonation, aromatic carboxylic acids, electroreduction, radical anions.

Previously¹ we demonstrated that one stage in the electroreduction (ER) of aromatic carboxylic acids in aprotic solvents is protonation of the radical anions (RA) formed by the original acid (self-protonation) (1).

$$AH^- + AH \xrightarrow{k_1} AH_2^+ + A^-$$
(1)

At the same time, as follows from theoretical and experimental studies^{2,3} of the reactivity of RA, the presence of electron-acceptor substituents in molecules of aromatic compounds favors the dimerization of their RA. This allows one to suggest that in the ER of aromatic carboxylic acids a process similar to the dimerization of RA of aromatic carbonyl derivatives³⁻⁶ (reaction (2)) can occur alongside reaction (1).

$$AH^{-} + AH^{-} \xrightarrow{k_2} ^{-}HA - AH^{-}$$
(2)

Process (2) has never been considered typical of the ER of aromatic carboxylic acids. The experimental proof of the possibility of such a reaction is of definite interest and might confirm the existing theoretical concepts²⁻³ about the reactivity of RA.

An aromatic carboxylic acid with a sufficiently high ratio of the rate constants for reactions (2) and (1), k_2/k_1 , is the subject of choice. The values of these constants can be estimated^{2,7} on the basis of data on the structure of the boundary MO (BMO) in the RA.

Results and Discussion

The results of our quantum-chemical calculations (CNDO/2) of benzoic (1), 1-naphthoic (2), and 9anthroic (3) acids and benzene, naphthalene, and anthracene acetyl derivatives show that the structures of the HOMO of the RA and the corresponding carboxylic and carbonyl compounds are qualitatively similar (Table 1). In particular, in both cases the wave function of the BMO for benzene, naphthalene, and anthracene derivatives has maximum amplitudes in positions 4, 4, and 9, respectively. Additionally, it follows from Table 1 that the dimerization of RA of aromatic carboxylic acids, like that of RA of the corresponding acetyl derivatives, can occur with the participation of either the carboxylic group carbon atom or the aromatic ring carbon atoms.

Table 1. Electron density ρ at reaction centers of aromatic carboxylic acids and acetyl derivatives

ρ1	ρ ₂	
0.222	0.150	
0.200	0.070	
0.212	0.038	
0.183	0.169	
0.194	0.070	
0.216	0.033	
	ρ1 0.222 0.200 0.212 0.183 0.194 0.216	$\begin{array}{c ccccc} \rho_1 & \rho_2 \\ \hline 0.222 & 0.150 \\ 0.200 & 0.070 \\ 0.212 & 0.038 \\ 0.183 & 0.169 \\ 0.194 & 0.070 \\ 0.216 & 0.033 \\ \end{array}$

Note. ρ_1 is the electron density at the C_{arom} atom; ρ_2 is the electron density at the C atom of the functional group.

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 1735–1738, October, 1993. 1066-5285/93/4210-1658 \$12.50 © 1994 Plenum Publishing Corporation Using the data of Table 1 and the parameters of the corresponding correlation equations,³ one can conclude that the ratios of the rate constants k_2/k_1 for 1, 2, and 3 are 0.32, 0.05, and 0.12, respectively. Therefore, it is anticipated that the formation of dimeric products is most probable in the ER of benzoic acid and will virtually not occur in the electrolysis of 1-naphthoic acid. The latter conforms with the results¹ of the constant potential electrolysis (CPE) of this compound.

The theoretical model³ employed for the radical anion reactions allows one to draw conclusions not only about the competition between the reactions (1) and (2), but about the regioselectivity of the dimerization as well. In particular, the use of the previously proposed⁸ method for the theoretical estimation of the yields of isomeric products shows that the dimerization of RA of 3, like that of RA of other anthracene derivatives, must result in a dimeric dianion of the "tail-to-tail" type.



However, the isolation of such dimers is unlikely, because the corresponding dimeric dianion is protonated and undergoes further reduction and destruction to form the initial compound and a dihydro derivative. The same processes occur in the cathodic dimerization of anthracene derivatives (AH) in the presence of proton donors^{9,10} (reaction (3)).



This also appears to explain the high yield of the dihydro derivative¹ in the CPE of 3 (70 %), which exceeds that expected (50 %).

At the same time in the dimerization of RA of 1, dimeric dianions of the "head-to-tail" and "tail-to-tail" types should be formed in approximately equal amounts.



Thus, the isolation of "head-to-tail" dimers in the CPE of 1 can serve as direct proof of the existence of the dimerization of RA of aromatic carboxylic acids.

In the ER of 1 under aprotic conditions (with Bu_4NClO_4 as the supporting electrolyte) significant amounts of resinous products were formed,¹ and 1 was the only identified substance (no more than 50 % of the initial amount). For this reason and taking into account the extreme instability of carbonyl (carboxyl) derivatives hydrogenated in the aromatic ring we worked up the solution after the electrolysis (dilution, acidification, extraction with ether) under an argon atmosphere, and only the product separation and identification stages were performed in air. These precautions allowed the isolation of a product identified by the mass spectrum (MW 228) as 4-(α -hydroxybenzyl)benzoic acid (5) from the reaction mixture after exhaustive electrolysis of the solution of 1. Its formation can be represented by Scheme 1,

Scheme 1



according to which dimeric ketocarboxylic acid (4) is an intermediate product. The electrolysis of 1 with a fixed (1 F/mole) amount of electricity was performed to check this assumption. In this case, the ¹H NMR spectrum of the dimer isolated from the reaction mixture was similar to that of 4-(α -hydroxybenzyl)benzoic acid 5, with the difference that the chemical shift of the two aromatic protons (in the ring with the carboxyl group) was 8.1 ppm (for 5 it is 8.0 ppm) and the signal for the methine

proton (for 5 it is at 5.88 ppm) was absent. In the IR spectrum of this dimer (solution in CHCl₃), the intense band at 1700 cm⁻¹ of the acid carbonyl was present along with a band at 1675 cm^{-1} which should be attributed to the conjugated ketone; the IR spectra of dimers 4 and 5 essentially differed in the intensity of the v(OH)vibrations (3610 $\,\mathrm{cm}^{-1}$). The comparison of the ¹H NMR and IR spectra of the mixture of dimers isolated after time-limited (O = 1 F/mole) and exhaustive (O = $3\div 4$ F/mole) electrolyses allows one to estimate the ratios of 4 and 5. In the first case, 4 predominates (2.5:1), in the second case, it is present only in trace amounts. The overall yield of the dimeric products does not exceed 25-30 % with respect to the consumed 1, and the absence of dihydro derivatives of 1 is due to their low stability.¹¹ As far as we know, this is the first example of the involvement of the carboxyl group as a reaction center in a dimerization reaction of the "headto-tail" type.

Previously it was mentioned¹ that the results of the theoretical analysis and the composition of the products of the CPE of **2** in DMF containing tetrabutylammonium perchlorate attest to the dominant role of reaction (1). Therefore, **2** is a convenient object for studies of the effect of the catholyte composition on this process. Chromatography of the ethereal extract of the solution after the CPE of **2** (Table 2) in DMF (or DMSO) yielded the following major electrolysis products: 1,4-dihydronaphthoic acid (6) (35 % with respect to the consumed **2**) and 1-naphthylenemethanol (7) (no more than 10 %), as well as unchanged **2** (45 %).

In the ¹H NMR spectrum of the crude product (ethereal extract), alongside the signals corresponding to 2 and 6 there were additional weak signals in the region of δ : 3.3–3.6; 6.5. The presence of these signals and their changes after isolation of specific fractions allow for the presence of isomers of 6 (up to ~10 %). If,

Table 2. Effect of the CPE conditions on the yield of 1,4-dihydronaphthoic acid (6) (E = -2.1 V relative to a saturated calomel electrode)

Ru	n Background (solvent)	n*	Recovery of 2 (%)	Yield of 6 (%)
1	0.1 <i>M</i> Bu ₄ NClO ₄ (DMF)	1.5	45	35
2	0.1 <i>M</i> Bu ₄ NClO ₄ (DMF- 5 % H ₂ O)	1.5	30	60
3	0.1 <i>M</i> Bu_4NClO_4 (DMF- 20 % H_2O)	2.2	-	70
4	0.1 <i>M</i> Bu ₄ NClO ₄ + 0.1 <i>M</i> LiClO ₄ (DMF- 5 % H ₂ O)	1.0	40	40

* The increase in the electron number (n) (runs 1 and 2; theoretical number $n \approx 1$) can be explained by the formation of compound 7, *i.e.*, by the reduction of the carboxyl group with consumption of $4e^{-1}$.

following the isolation of 2, 6, and 7, the chromatographic column is eluted further, an additional amount of a mixture of 2 and 6 (up to 15 %) can be isolated. This can be explained by the decomposition of dimeric intermediates formed in small amounts.

The signals at 6.5 ppm together with the additional aromatic signals in the ¹H NMR spectrum of the crude product also attest to the possible existence of such intermediates.

When the water content is 20 %, the yield of **6** increases to 70 %, probably due to the proton-donor properties of H₂O. In this case, in the ¹H NMR spectrum of the crude product minor signals corresponding to dimeric intermediates are observed. The signals corresponding to **2** appear with time, which can be the consequence of both the decomposition of dimeric intermediates and the aromatization of **6** during the exposure of the solutions to air. The presence of Li⁺ ions in solutions with 5 % H₂O decreases the yield of **6** (see Table 2, runs 2 and 4) due to the decrease in the protonation rate of RA ion pairs with Li⁺ cations as compared with the protonation of free RA. The increase in the amount of **2** after isolation attests to the decomposition of dimeric intermediates.

The comparison of the experimental results obtained for the ER of aromatic acids (a "head-to-tail" dimer for 1, decomposition products for 2, and the complete absence of dimers for 3) allows one to suggest that the dimerization reaction (2), whose rate under electrolysis conditions must increase (high concentrations of a depolarizer) continues further through the route corresponding to reaction (3).

Experimental

Experimental conditions, apparatus, and workup of solutions have been described previously.¹ The data on identification of **6** and 9,10-dihydroanthracene-9-carboxylic acid are also given in Ref. 1. IR spectra were recorded on a Specord M-80 spectrometer (pellets with KBr). ¹H NMR spectra were obtained on a Bruker-250 instrument (CCl₄, CDCl₃).

The ethereal extract of the solution after the electrolysis of 1 was treated with an ethereal solution of freshly prepared diazomethane, and after the removal of ether the residue was chromatographed using a hexane—ether (2:1) mixture to give methyl 4-(α -hydroxybenzyl)benzoate. ¹H NMR (CDCl₃, δ): 3.9 (s, 3 H, OCH₃); 5.88 (s, 1 H, CH); 7.3 (m, 5 H, Ar); 7.5–8.0 (H, Ar).

References

- 1. A. S. Mendkovich, O. Hammerich, T. Ya. Rubinskaya, and V. P. Gultyai, Acta Chem. Scand., 1991, 45, 644.
- V. P. Gultyai and A. S. Mendkovich, J. Electroanal. Chem., 1983, 145, 201.
- 3. A. S. Mendkovich and V. P. Gultyai, *Teoreticheskie osnovy* khimii organicheskikh anion-radicalov [Theoretical Fundamentals of the Organic Radical Anion Chemistry], Nauka, Moscow, 1990, 152 (in Russian).

1661

- 4. V. P. Gultyai, A. S. Mendkovich, and T. Ya. Rubinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1576 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1987, 36, 1455 (Engl. Transl.)].
- V. P. Gultyai, T. Ya. Rubinskaya, and A. S. Mendkovich, Izv. Akad. Nauk SSSR, Ser. Khim., 1991, 433 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1991, 40, 372 (Engl. Transl.)].
- V. P. Gultyai, T. Ya. Rubinskaya, A. S. Mendkovich, and A. I. Rusakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2812 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, 36, 2609 (Engl. Transl.)].
- A. S. Mendkovich, A. I. Rusakov, G. S. Mironov, and V. P. Gultyai, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987,

106 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1987, 36, 90 (Engl. Transl.)].

- 8. A. S. Mendkovich, *Elektrokhimiya*, 1992, **28**, 485 [*Russ. Electrochem.*, 1992, **28** (Engl. Transl.)].
- 9. A. S. Mendkovich, L. V. Mikhalchenko, and V. P. Gultyai, J. Electroanal. Chem., 1987, 224, 273.
- 10. V. P. Gultyai, N. K. Lisitsina, A. V. Ignatenko, and A. S. Mendkovich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 873 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 771 (Engl. Transl.)].
- 11. M. E. Kuchne and B. F. Lambert, Org. Synth., 1963, 43, C22.

Received January 15, 1993

Preparation and reactivity of metal-containing monomers 33*. Investigation of a cluster-type monomer [Fe₃O(OCOCH=CH₂)₆]OH and its polymerization product by IR, XPS, Mössbauer, and mass spectroscopy

Yu. M. Shul'ga, * O. S. Roshchupkina, G. I. Dzhardimalieva, I. V. Chernushevich, A. F. Dodonov, Yu. V. Baldokhin, P. Ya. Kolotyrkin, A. S. Rozenberg, and A. D. Pomogailo

> Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (095) 265 5714

A new cluster-type monomer $[Fe_3O(OCOCH=CH_2)_6]OH \cdot 3H_2O$ was synthesized by the reaction of acrylic acid with freshly prepared iron hydroxide. The monomer was characterized by various physicochemical methods. It has been shown that the acid residues are bound to the metal atoms through carboxyl groups in a bridge-like or bidentate fashion, and the double bond does not participate in the coordination. The mechanism of thermal fragmentation of the $[Fe_3O(OCOCH=CH_2)_6]^+$ cluster was studied. It was demonstrated that the radical polymerization of this monomer involved bidentate acrylate groups. No reduction of Fe³⁺ during the polymerization was observed.

Key words: iron acrylate, metal-containing monomers and polymers, X-ray photoelectron, Mössbauer, IR, and mass spectra, structure.

Polymerization of metal-containing monomers may be accompanied by a number of side processes associated with redox transitions of the metal ion, changes in the structure of its nearest coordination sphere, and others. For example, it has been shown¹ that during the polymerization of cupric acrylate, $Cu(Acr)_2$ (Acr stands for OCOCH=CH₂), Cu^{2+} ions are partly reduced to Cu^+ . It has been suggested² that the reduction of metal ions during the polymerization of these monomers is due to their competing interaction with free radicals. This interaction is in turn determined by the standard redox potential (E_0) for an $M^{n+}+e^-/M^{(n-1)+}$ pair. In the light of this suggestion, one might expect that in the case of polymerization of Fe^{III} acrylate the degree of reduction would be even higher than in the case of Cu(Acr)₂, since E_0 for the Fe³⁺ \rightarrow Fe²⁺ transition in an aqueous solution is 0.77 V (for the Cu²⁺ \rightarrow Cu⁺ transition³ $E_0 = 0.16$ V).

In this paper we present the results of a study of Fe^{III} acrylate, $[Fe_3O(OCOCH=CH_2)_6]OH$, and the product of its polymerization by means of X-ray photoelectron

1066-5285/93/4210-1661 \$12.50 © 1994 Plenum Publishing Corporation

^{*} For part 32 see Ref. 1.

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 1739-1743, October, 1993.