

# Self-Protonation Reaction of Simple Aromatic Carboxylic Acids During Voltammetric Reduction in Dimethyl Sulfoxide<sup>#</sup>

Andrej S. Mendkovich,<sup>a,\*</sup> Ole Hammerich,<sup>b,\*</sup> Tamara Ya. Rubinskaya<sup>a</sup> and Vadim P. Gulyai<sup>a</sup>

<sup>a</sup>N. D. Zelinsky Institute of Organic Chemistry, The USSR Academy of Sciences, Leninsky Prospect 47, Moscow, USSR and

<sup>b</sup>Department of Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Mendkovich, A. S., Hammerich, O., Rubinskaya, T. Ya. and Gulyai, V. P., 1991. Self-Protonation Reaction of Simple Aromatic Carboxylic Acids During Voltammetric Reduction in Dimethyl Sulfoxide. – Acta Chem. Scand. 45: 644–651.

The electrochemical behavior of three simple aromatic carboxylic acids, benzoic acid (PhCOOH), 1-naphthoic acid (NphCOOH) and 9-anthroic acid (AnCOOH) has been studied in dimethyl sulfoxide. The results of cyclic voltammetry and derivative cyclic voltammetry (DCV) suggest that the initial electrode process was formation of the corresponding anion radical, which for NphCOOH and AnCOOH, and possibly also for PhCOOH, was protonated by the substrate in a so-called self-protonation step [eqn. (i), Ar = aryl] followed by further reaction of ArHCOOH<sup>•</sup>.



The coulometric *n*-values determined by constant current coulometry were observed to be close to unity in agreement with the stoichiometry of the overall reaction, eqn. (ii), where ArH<sub>2</sub>COO<sup>-</sup> is the base corresponding to the dihydrogenated product, ArH<sub>2</sub>COOH. The latter was isolated in good yield together with ArCOOH after preparative electrolyses of NphCOOH and AnCOOH.



The kinetics of reaction (i) were studied by DCV for NphCOOH and AnCOOH. The rate constants, *k<sub>i</sub>*, obtained were 4.7 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> (NphCOOH) and 2.9 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> (AnCOOH), respectively.

Definitive conclusions regarding PhCOOH could not be drawn. The voltammetric reduction stayed chemically irreversible at voltage sweep rates up to 1000 V s<sup>-1</sup> and only polymeric products were isolated after preparative electrolysis.

Reactions during which an anion radical is protonated by substrate, the so-called self-protonation reactions, have been the subject of much research during the last two decades.<sup>1–10</sup> The compounds that have been investigated so far include carbon acids such as indenenes,<sup>1,2</sup> fluorenes<sup>3</sup> and 4,5-methylenephenanthrene,<sup>1,4,5</sup> nitrogen acids such as phthalimide<sup>6,7</sup> and nitroimidazoles,<sup>8</sup> and oxygen acids such as nitrophenols.<sup>1,9,10</sup> Related to these reactions is the electrochemical reduction of 1,3- and 1,4-diketones<sup>11–14</sup> during which protonation of intermediates by substrate is a characteristic feature of the mechanism. Aromatic carboxylic acids, which may be considered the most natural object of this type of research, have not received much attention. Moreover, the electrochemical reduction of simple unsubstituted aromatic carboxylic acids appears only to have been studied in some detail for benzoic acid.<sup>15–17</sup>

\* Presented at the 15th Sandbjerg Meeting on Organic Electrochemistry, June 1990 and SCAN-ELCHEM-90, Copenhagen, October, 1990.

\* To whom correspondence should be addressed.

The aim of the present work was to study the electrochemical behavior of some typical unsubstituted aromatic carboxylic acids under aprotic conditions and to investigate whether the self-protonation mechanism is operative for these compounds. The experimental work was carried out with dimethyl sulfoxide (DMSO) solutions of benzoic acid (PhCOOH), 1-naphthoic acid (NphCOOH) and 9-anthroic acid (AnCOOH).

## Results and discussion

**Cyclic voltammetry (CV).** The cyclic voltammogram of a 2.5 mM solution of AnCOOH in DMSO at a voltage sweep rate (*v*) of 10 V s<sup>-1</sup> is shown in Fig. 1(a) (full line). The first reduction peak, R<sup>1</sup>, was chemically irreversible at this sweep rate, but an anodic peak, O<sup>1</sup>, corresponding to R<sup>1</sup> began to emerge at sweep rates higher than 20 V s<sup>-1</sup> and was fully developed at *v* = 1000 V s<sup>-1</sup> as shown also in Fig. 1(a) (broken line). Thus, at *v* ≤ 10 V s<sup>-1</sup> the peak R<sup>1</sup> appears to reflect the formation of the anion radical, AnCOOH<sup>•-</sup>, followed by further reaction. Continuation of

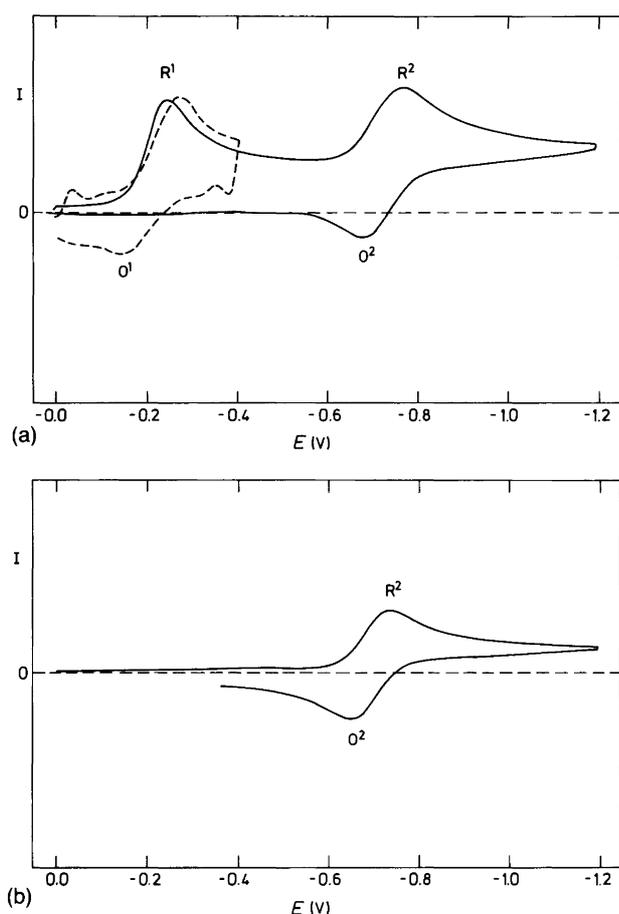
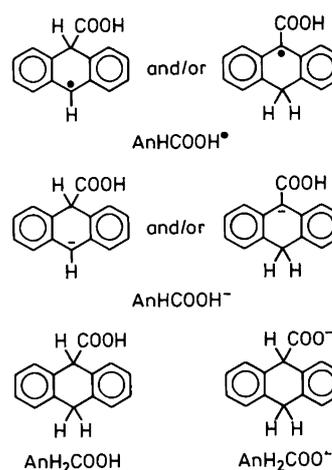


Fig. 1. (a) Cyclic voltammogram of 9-anthroic acid (2.5 mM) in DMSO containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) at  $\nu = 10 \text{ V s}^{-1}$  (—) and  $\nu = 1000 \text{ V s}^{-1}$  (-----);  $T = 294 \text{ K}$ . The current amplification at  $\nu = 1000 \text{ V s}^{-1}$  was 10 times lower than that at  $\nu = 10 \text{ V s}^{-1}$ . (b) Same as (a) at  $\nu = 10 \text{ V s}^{-1}$ , but after the addition of a slight excess of  $\text{Bu}_4\text{NOH}$  (40% solution in water).

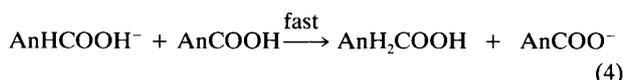
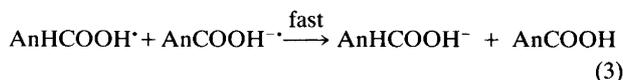
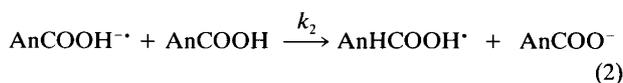
the voltage sweep at  $\nu = 10 \text{ V s}^{-1}$  revealed a second reduction peak,  $\text{R}^2$ , the anodic counterpart of which,  $\text{O}^2$ , is also seen in Fig. 1(a). The origin of these peaks was demonstrated by addition of an excess of strong base,  $\text{Bu}_4\text{NOH}$ , to the voltammetry solution by which  $\text{AnCOOH}$  was converted completely into the corresponding anion,  $\text{AnCOO}^-$ . The voltammogram of the resulting solution [Fig. 1(b)] showed that  $\text{R}^2$  and  $\text{O}^2$  were associated with the quasi-reversible one-electron reduction of  $\text{AnCOO}^-$  to the dianion radical,  $\text{AnCOO}^{2-\cdot}$ . The peak separation,  $E_p(\text{O}^2) - E_p(\text{R}^2)$ , at  $\nu = 10 \text{ V s}^{-1}$  was found to be 90 mV or approximately 30 mV larger than that for a reversible process. The details of the quasi-reversible reduction of  $\text{AnCOO}^-$  and other related anions are presently under investigation.<sup>18</sup>

The fact that the peaks  $\text{R}^2$  and  $\text{O}^2$  were detectable in the voltammogram for  $\text{AnCOOH}$  even before addition of the strong base suggested that the reaction following the initial one-electron transfer was protonation of  $\text{AnCOOH}^{\cdot-}$  by  $\text{AnCOOH}$  resulting in the formation of equimolar amounts of  $\text{AnCOO}^-$  and the intermediate free radical,



Scheme 1.

$\text{AnHCOOH}^{\cdot}$  (see Scheme 1 for structures). The structure of  $\text{AnHCOOH}^{\cdot}$  is similar to those of the radicals generally formed during reduction of aromatic hydrocarbons in the presence of suitable proton donors,<sup>19</sup> and the remaining reaction sequence leading to the final product,  $\text{AnH}_2\text{COOH}$ , no doubt includes a series of chemical steps similar to those for an aromatic hydrocarbon, for example anthracene.<sup>19-22</sup> Thus, we suggest that the voltammetric reduction of  $\text{AnCOOH}$  in DMSO is described by the reaction sequence (1)–(4), with (2) being rate determining. Because of the relatively low rate of reaction (2), the homogeneous reduction of  $\text{AnHCOOH}^{\cdot}$ , eqn. (3), dominates the electrochemical reduction,<sup>23</sup>  $\text{AnHCOOH}^{\cdot} + e^- \rightarrow \text{AnHCOOH}^-$ , which for that reason will be neglected in the mechanistic discussion.



Mechanism (1)–(4) is similar to that proposed for other self-protonation reactions,<sup>1</sup> but is not a complete description of the voltammetric reduction of  $\text{AnCOOH}$ , and  $\text{ArCOOH}$  in general, as discussed later.

In the sweep rate range  $0.1\text{--}10 \text{ V s}^{-1}$  a pre-peak appeared as a shoulder in front of the second reduction peak,  $\text{R}^2$  (Fig. 2). This pre-peak, which is absent in the voltammogram of  $\text{AnCOO}^-$  in the same sweep rate range, most

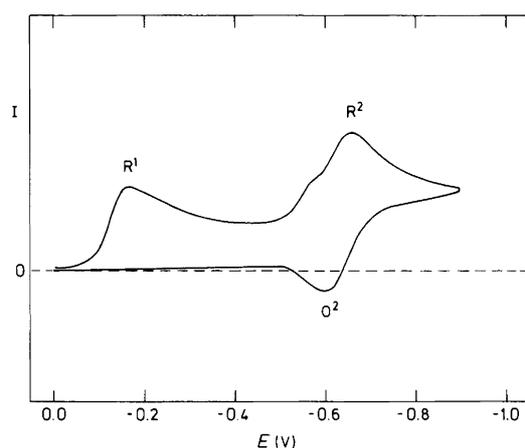


Fig. 2. Cyclic voltammogram of 9-anthroic acid (1 mM) in DMSO containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) at  $\nu = 1 \text{ V s}^{-1}$  and  $T = 294 \text{ K}$ .

likely originates from the reaction of  $\text{AnCOO}^{2-}$  with  $\text{AnCOOH}$  and  $\text{AnH}_2\text{COOH}$ .<sup>24</sup> Thus, the pre-peak reflects a kinetic phenomenon rather than the reduction of an intermediate.<sup>25-27</sup>

Essentially the same voltammetric behavior was observed for  $\text{NphCOOH}$ , except that voltage sweep rates above  $100 \text{ V s}^{-1}$  were required for the observation of the oxidation current for  $\text{NphCOOH}^-$ , and the reduction of  $\text{NphCOOH}$  seems to follow the same mechanism as that for  $\text{AnCOOH}$ .

The reduction of  $\text{PhCOOH}$  stayed irreversible even at  $\nu = 1000 \text{ V s}^{-1}$  and conclusions regarding the reduction mechanism could not be drawn from the CV experiments.

It has been argued<sup>28</sup> that  $\text{ArCOOH}^-$  are improbable intermediates in the voltammetric reductions of  $\text{ArCOOH}$  and that the mechanism more likely involves the reduction of protons, as observed for other acids under non-aqueous conditions.<sup>15,29,30</sup> However, we wish to emphasize that there is good experimental evidence for the existence of  $\text{ArCOOH}^-$ ;  $\text{PhCOOH}^-$ , for example, has been prepared

Table 1. Voltammetric peak potentials,  $E_p$ , for the reduction of aromatic carboxylic acids,  $\text{ArCOOH}$ , and methyl esters,  $\text{ArCOOMe}$ , in dimethyl sulfoxide.<sup>a</sup>

Compound	Peak	$-E_p/\text{V vs. Ag/Ag}^+$
$\text{PhCOOH}$	$\text{R}^1$	2.15
$\text{PhCOOMe}$	$\text{R}^1$	2.24
$\text{NphCOOH}$	$\text{R}^1$	1.82
	$\text{R}^2$	2.45
$\text{NphCOOMe}$	$\text{R}^1$	1.87
$\text{AnCOOH}$	$\text{R}^1$	1.48
	$\text{R}^2$	1.96
$\text{AnCOOMe}$	$\text{R}^1$	1.53 <sup>b</sup>

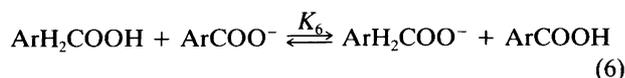
<sup>a</sup>In solvent containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M);  $\nu = 10 \text{ V s}^{-1}$ ,  $T = 294 \text{ K}$ . <sup>b</sup>Value corrected for the kinetic shift caused by the dimerization of the anion radical (see the text).

in solution by pulse radiolysis<sup>31,32</sup> or by reduction with solvated electrons<sup>33</sup> and has been characterized spectroscopically.<sup>31</sup> In addition, we find it highly unlikely that electrode processes that approach reversibility at voltage sweep rates less than  $1000 \text{ V s}^{-1}$  involve the reduction of protons. Another piece of evidence that supports our suggestion of initial formation of  $\text{ArCOOH}^-$  is found in Table 1, which summarizes the voltammetric peak potentials for the reduction of  $\text{ArCOOH}$  and the corresponding methyl esters,  $\text{ArCOOMe}$ .

Owing to the almost identical Hammett  $\sigma$ -values for the  $\text{COOH}$  and  $\text{COOMe}$  groups,<sup>34</sup> the exchange of the hydrogen atom in  $\text{COOH}$  with a methyl group is expected to result only in minor changes in the  $E_p$  values for reversible one-electron reduction. Inspection of the experimental data in Table 1 shows that the acids are slightly more easily reduced than the corresponding methyl esters. The observed difference in  $E_p$  for related pairs of compounds is 90 mV for  $\text{Ar} = \text{Ph}$  and only 50 mV for  $\text{Ar} = \text{Nph}$  or  $\text{An}$ . However, not all of the compounds in Table 1 undergo simple one-electron transfer processes. The voltammetric reduction of alkyl esters derived from aromatic carboxylic acids in general, and of  $\text{PhCOOMe}$  and  $\text{NphCOOMe}$  in particular, is known to result in the reversible formation of the corresponding anion radicals under aprotic conditions,<sup>35-41</sup> but the ester,  $\text{AnCOOMe}$ , is an exception in this respect since  $\text{AnCOOMe}^-$  dimerizes within the timescale of slow sweep CV, analogously to the anion radicals of other anthracene derivatives substituted with electron-withdrawing groups in the 9-position.<sup>41,42</sup> The rate constant for dimerization is of the order of  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and accordingly, the peak potential for  $\text{AnCOOMe}$  recorded during CV at  $C_{\text{AnCOOMe}}^\infty = 1 \text{ mM}$  and  $\nu = 10 \text{ V s}^{-1}$  will be shifted by approximately +0.02 V relative to that for the strictly reversible case.<sup>43</sup> The value of  $E_p$  for  $\text{AnCOOMe}$  given in Table 1 has been corrected for this shift. The values of  $E_p$  for the carboxylic acids are also affected by the kinetics of the follow-up reactions. However, only moderate voltage sweep rates were necessary to outrun the follow-up reactions for  $\text{NphCOOH}$  and  $\text{AnCOOH}$  and therefore the shift was deemed to be small, probably in the range +0.02 to +0.04 V. This means that the values of  $E_p$  estimated for the reversible one-electron reduction of  $\text{NphCOOH}$  and  $\text{AnCOOH}$ , and probably also for  $\text{PhCOOH}$ , are in fact very close to those for the corresponding methyl esters. We believe that this provides convincing supplementary evidence for our suggestion that the first event during voltammetric reduction of compounds of the general structure,  $\text{ArCOOH}$ , is indeed the formation of the corresponding anion radical and not the reduction of protons.

**Coulometry and preparative electrolysis.** The stoichiometry of a reaction sequence involving only steps (1)–(4) is given by eqn. (5), which predicts a coulometric  $n$ -value of 2/3. However, the products,  $\text{ArH}_2\text{COOH}$  and  $\text{ArCOO}^-$  exist in solution in fast equilibrium with  $\text{ArH}_2\text{COO}^-$  and

ArCOOH, eqn. (6), and for this reason a third of the substrate consumed in reactions (1)–(4) will be regenerated during coulometry or any other kind of exhaustive electrolysis. As a result of this, the stoichiometric equation changes to (7) from which it is seen that a coulometric  $n$ -value of unity rather than  $2/3$  is to be expected for the reaction.



The results of constant current coulometry<sup>44,45</sup> are shown in Table 2 and it is seen that the observed values of  $n$  are indeed very close to unity for all three acids. This is in agreement with the interpretation of the voltammetric results for NphCOOH and AnCOOH given above, but cannot as such be taken as additional support for the proposed mechanism, since an  $n$ -value of unity would also be expected for a mechanism involving reduction of protons to molecular hydrogen,  $2 \text{ArCOOH} + 2 e^- \rightarrow 2 \text{ArCOO}^- + \text{H}_2$ .

The product distributions obtained after preparative electrolyses of NphCOOH and AnCOOH were as expected from the proposed mechanism. The details are given in the Experimental section. The analysis showed that the products obtained for NphCOOH after acidification were essentially a 1:1 mixture of NphH<sub>2</sub>COOH and NphCOOH in agreement with eqn. (7) and mechanism (1)–(4), (6). For AnCOOH the yield of AnH<sub>2</sub>COOH was somewhat higher (70%) and the amount of AnCOOH recovered considerably smaller than predicted from eqn. (7), which corresponds to a coulometric  $n$ -value larger than unity. At first glance this may seem inconsistent with the value, 0.99, obtained by constant current coulometry (Table 2), but the phenomenon that experiments carried

out at different time scales may result in different  $n$ -values is not unusual in electrochemistry.<sup>44</sup> In the present case, the difference is most probably related to the problem of keeping the concentration of water in the solvent, during a lengthy preparative electrolysis, at the same low level as during a constant current coulometry experiment that takes five to six minutes. Thus, the high yield of AnH<sub>2</sub>COOH appears to result from partial protonation of AnCOO<sup>-</sup> by residual water followed by reduction of the resulting AnCOOH. Dimeric products were not observed for any of the two acids.

The interpretation of the results from preparative electrolysis of PhCOOH were less straightforward since the reduction of this compound resulted only in formation of polymeric products which could not be identified unambiguously.

**Kinetics and reaction orders.** The kinetics of the self-protonation reactions for NphCOOH and AnCOOH were studied by derivative cyclic voltammetry (DCV).<sup>44,46</sup> The analysis of a reaction scheme including only steps (1)–(4) is straightforward and results in rate laws (8)–(11) assuming reaction (2) to be rate determining and the validity of the steady-state approximation for the two transient species, ArHCOOH\* and ArHCOOH<sup>-</sup>.<sup>20-22</sup>

$$d[\text{ArCOOH}]/dt = -k_2[\text{ArCOOH}][\text{ArCOOH}^{\cdot-}] \quad (8)$$

$$d[\text{ArCOOH}^{\cdot-}]/dt = -2k_2[\text{ArCOOH}][\text{ArCOOH}^{\cdot-}] \quad (9)$$

$$d[\text{ArCOO}^-]/dt = 2k_2[\text{ArCOOH}][\text{ArCOOH}^{\cdot-}] \quad (10)$$

$$d[\text{ArH}_2\text{COOH}]/dt = k_2[\text{ArCOOH}][\text{ArCOOH}^{\cdot-}] \quad (11)$$

However, ArCOOH, ArCOO<sup>-</sup>, and ArH<sub>2</sub>COOH also participate, as already pointed out, in equilibrium (6), the equilibrium constant of which,  $K_6$ , is not known. The question is now to what extent the magnitude of  $K_6$  influences

Table 2. Coulometric  $n$ -values, values of the rate constant for self-protonation,  $k_2$ , and reaction orders,  $R_{AB}$ , for the reduction of aromatic carboxylic acids in dimethyl sulfoxide.<sup>a</sup>

Compound	Coulometric $n$ -value <sup>b</sup>	$k_2 \times 10^{-6}$ $\text{M}^{-1} \text{s}^{-1}$	$R_{AB}$ <sup>c</sup>
PhCOOH	$0.93 \pm 0.02$	— <sup>d</sup>	— <sup>d</sup>
NphCOOH	$1.06 \pm 0.03$	$4.7 \pm 0.9$ <sup>e</sup>	$1.95 \pm 0.16$
AnCOOH	$0.99 \pm 0.03$	$2.9 \pm 0.3$ <sup>e</sup>	$2.00 \pm 0.10$

<sup>a</sup>In solvent containing Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M);  $T = 294$  K.

<sup>b</sup>Determined by constant current coulometry. <sup>c</sup>Reaction order in  $[\text{ArCOOH}] + [\text{ArCOOH}^{\cdot-}]$  defined as  $1 + d \log v_{0.5} / d \log C_{\text{ArCOOH}}^{\circ}$ .<sup>47</sup>

<sup>d</sup>Not measurable. <sup>e</sup>Evaluated from  $v_{0.5}$  measurements assuming  $K_6 = \infty$  (see the text). The uncertainty in the rate constants is mainly caused by the necessity to apply rather high voltage sweep rates during the measurements.

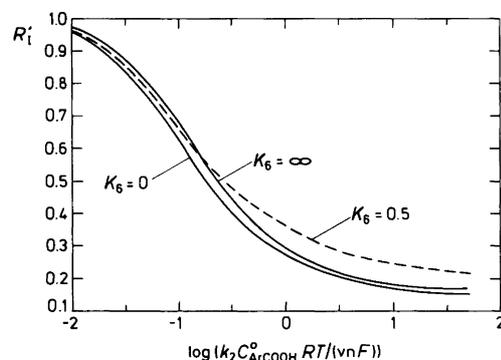


Fig. 3. Derivative cyclic voltammetry working curves for mechanism (2)–(4), (6) for  $K_6 = 0.5$  (-----) and the two limiting cases,  $K_6 = 0$  and  $K_6 = \infty$  (—).

the kinetic data for a particular value of  $k_2$ . In order to answer this question a series of calculations, during which  $k_2$  and  $K_6$  were varied systematically, were carried out by digital simulation (see the Experimental section). The results of these calculations are shown in Fig. 3 as working curves for the two limiting cases,  $K_6 = 0$  and  $K_6 = \infty$ , (full lines) and one intermediate case,  $K_6 = 0.5$ , (broken line).

It should be noted that the working curve for  $K_6 = 0.5$  is not located between those for the two limiting cases. The reason for this is that the DCV method is based on analysis of the ratio of the maximum positive and negative slopes of the cyclic voltammogram and thereby reflects the changing shape of the voltammogram in passing from  $K_6 = 0$  to  $K_6 = \infty$ . However, the working curves for  $0 < K_6 < \infty$  are not sufficiently different in shape to allow for the simultaneous evaluation of  $k_2$  and  $K_6$ . The maximum error introduced in  $k_2$  by using the working curve for  $K_6 = \infty$ , independent of the real value of  $K_6$ , was estimated to be only 26% when the evaluation of  $k_2$  was based on measurements of  $v_{0.5}$ .

As a final test of the validity of rate law (8) a series of measurements were carried out for NphCOOH and AnCOOH to determine the reaction order in  $[\text{ArCOOH}] + [\text{ArCOOH}^{\cdot-}]$ ,  $R_{A/B} = 1 + d \log v_{0.5} / d \log C_{\text{ArCOOH}}^{\cdot-}$ ,<sup>47</sup> which for rate law (8), is predicted to have a value of two. The results, which are shown in Table 2, demonstrate that  $R_{A/B}$  for both compounds is in agreement with the expectation within the experimental error.

The values of  $k_2$  for NphCOOH and AnCOOH determined as described above are shown in Table 2 and it is seen that the two rate constants differ only by a factor of 1.6. We are not aware of data for the  $pK_A$  values of NphCOOH and AnCOOH in DMSO, but the values are likely to be very similar as judged from the corresponding values measured in water: 3.69 and 3.65, respectively.<sup>48</sup> The small value of the ratio,  $k_2(\text{NphCOOH})/k_2(\text{AnCOOH})$ , appears, therefore, to reflect that the kinetic basicities of  $\text{NphCOOH}^{\cdot-}$  and  $\text{AnCOOH}^{\cdot-}$  are also very similar. At first glance this may seem a surprising conclusion considering, for example, that the rate constant for protonation of the naphthalene anion radical by phenol in DMF or DMSO is approximately a factor of 30 larger than that for protonation of the anthracene anion radical.<sup>49,50</sup> This difference in the relative reactivity of these closely related anion radical systems may be rationalized within the formalism of perturbation molecular orbital (PMO) theory.<sup>51</sup> The self-protonation reactions may be described in PMO theory as involving the interaction of two degenerate molecular orbitals (first-order perturbation) and accordingly, the rate is controlled only by electron density. Quantum chemical calculations have shown that the ratio of the frontier electron densities at the reaction centers of  $\text{ArCOOH}^{\cdot-}$  and  $\text{ArCOOH}$  is very close to unity, the values being 1.06 and 1.07 for  $\text{Ar} = \text{Nph}$  and  $\text{An}$ , respectively,<sup>41</sup> which predicts very similar rates for the two systems, as observed. On the other hand, the rates of protonation the naphthalene and anthracene anion radicals by PhOH depend strongly on the energy gap between the frontier molecular orbitals of the

anion radical and PhOH (second-order perturbation). Taking into account the significant difference between the electron affinity of naphthalene and anthracene, which amounts<sup>52</sup> to 0.4 eV or approximately 9 kcal mol<sup>-1</sup>, a pronounced difference in the kinetic basicity of the corresponding anion radicals is to be expected, in agreement with the experimental observations. More detailed theoretical studies of the kinetics of protonation of anion radicals are in progress.<sup>53</sup>

Finally we would like to comment on the competition between protonation and dimerization of  $\text{AnCOOH}^{\cdot-}$ . As mentioned above it is well known that the electrochemical reduction of AnCOOMe is followed by dimerization of  $\text{AnCOOMe}^{\cdot-}$  with  $k_{\text{dim}} \approx 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>41</sup> and on the basis of arguments already presented,  $\text{AnCOOH}^{\cdot-}$  may be supposed to undergo dimerization with a rate constant close to this value, which is only a factor of three smaller than  $k_2$  for this compound. Therefore, it might be expected that the value of  $k_2$  is affected by competing dimerization. However, it should be emphasized that the value of  $k_{\text{dim}}$  given for  $\text{AnCOOH}^{\cdot-}$  is only a rough estimate and the total absence of dimeric products after preparative electrolysis indicates that the value of  $k_2$  given for AnCOOH is not affected by competing dimerization.

## Experimental

*Reagents, electrodes, cells and instrumentation for kinetic measurements.* 1-Naphthoic acid (Fluka, *purum*) was used as received. 9-Anthroic acid was either from Aldrich Chemie (99%) or prepared from the Grignard reagent of 9-bromoanthracene (Fluka, *pract.*) by reaction with solid carbon dioxide. The crude product was recrystallized several times from ethanol-water (3:2), (m.p. 212–214°C, lit.<sup>54</sup> m.p. 217–220°C; anal. C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>: C, H). Tetrabutylammonium hexafluorophosphate was prepared from tetrabutylammonium hydroxide (Aldrich Chemie) and hexafluorophosphoric acid (Aldrich Chemie, 60% solution in water) analogously to the procedure described earlier for tetrabutylammonium tetrafluoroborate.<sup>20</sup> The solutions of tetrabutylammonium hexafluorophosphate (0.1 M) in dimethyl sulfoxide (Fluka, *purum*) were passed through a column filled with neutral alumina (Woelm, W200) immediately before the measurements were made.

The electrodes, cells and instrumentation were the same as previously reported,<sup>20</sup> except that the current-voltage converter was a PAR model 276.

The value of  $E_{\text{sw}} - E^\circ$ , where  $E_{\text{sw}}$  is the potential at which the voltage sweep is reversed, was -0.2 V in order to avoid interference from the further reduction of  $\text{ArCOO}^{\cdot-}$  to  $\text{ArCOO}^{2-\cdot}$  (see the text).

*Coulometry.* Constant current (25 mA) coulometry was carried out under nitrogen in a cell divided by a sintered glass disk (G3) at a mercury pool cathode and a platinum gauze anode as described elsewhere.<sup>44,45</sup> The amount of substrate used in these experiments was 0.1 mmol.

*Preparative electrolyses.* Constant potential reductions of 1-naphthoic acid were carried out at  $-2.0$  V vs. a saturated calomel electrode (SCE) in a cell in which the anodic and cathodic compartments were separated by a ceramic membrane. The potentiostat was a PI-50-1 (USSR). The cathode was a mercury pool ( $20 \text{ cm}^2$ ) and the anode was a Pt-gauze. The SCE was connected to the cell through a salt bridge containing the solvent (DMSO) and the supporting electrolyte ( $\text{Bu}_4\text{NClO}_4$ ,  $0.1 \text{ M}$ ). After the passage of  $1.5 \text{ F}$ , the first wave of the starting material had disappeared and the electrolysis was stopped. The catholyte was diluted by water and acidified to  $\text{pH} = 3$ . The mixture was extracted with diethyl ether. After evaporation of the ether, the residue was chromatographed on a column filled with silica gel (mesh 100–140) by elution with hexane–diethyl ether (2:1). Two products were isolated, 1-naphthoic acid (yield: 45 %) and 1,4-dihydro-1-naphthoic acid (yield: 35 %). The yields are based on the initial amount of 1-naphthoic acid. It should be noted that the theoretical yields are only 50 % for each compound according to the stoichiometry of the reaction (see the text).  $^1\text{H}$  NMR data of 1,4-dihydro-1-naphthoic acid ( $\text{CDCl}_3$ , Bruker 250 MHz):  $\delta$  3.6 (2 H), 4.6 (1 H), 6.0–6.2 (2 H), 7.3 (4 H), 11.5 (1 H). The spectrum was in accord with one reported elsewhere.<sup>55</sup> Essentially the same procedure was followed for the reduction of 9-anthroic acid except that the working potential for this compound was  $-1.8$  V vs. SCE. The yield of the crude product was close to 70 % and was shown by  $^1\text{H}$  NMR spectroscopy to consist of 9,10-dihydro-9-anthroic acid together with trace amounts of the 9-anthroic acid, anthracene, 9,10-dihydroanthracene and anthraquinone. Not even traces of dimeric products were observed.  $^1\text{H}$  NMR data of 9,10-dihydro-9-anthroic acid ( $\text{CD}_3\text{COCD}_3$ , Bruker 250 MHz):  $\delta$  3.85–3.95 (1 H), 4.25–4.35 (1 H), 4.95 (1 H), 7.25–7.45 (8 H).

*Digital simulation.* The theoretical data for mechanism (1)–(4), (6), with equilibrium (6) being fast and reversible, were obtained by application of an explicit formulation of the diffusion problem followed by evaluation of the concentration changes caused by reactions (2)–(4), (6) in each time step and each volume element.<sup>56</sup> The treatment of the homogeneous kinetic problem was dependent on the magnitude of  $K_6$ .

For the general case,  $0 < K_6 < \infty$ , the concentration changes associated with reactions (2)–(4) were evaluated initially by application of the integrated rate law<sup>20,57</sup> followed by an equilibrium treatment of reaction (6). The rate laws (8)–(11) are given in dimensionless notation by eqns. (12)–(15), in which the parameters have the following significance:

$$\begin{aligned} a &= [\text{ArCOOH}]/C_{\text{ArCOOH}}^\circ, \\ b &= [\text{ArCOOH}^-]/C_{\text{ArCOOH}}^\circ, \\ c &= [\text{ArCOO}^-]/C_{\text{ArCOOH}}^\circ, \\ d &= [\text{ArH}_2\text{COOH}]/C_{\text{ArCOOH}}^\circ, \\ \lambda_2 &= k_2 C_{\text{ArCOOH}}^\circ RT/(vnF) \text{ and} \\ \tau &= tvnF/(RT). \end{aligned}$$

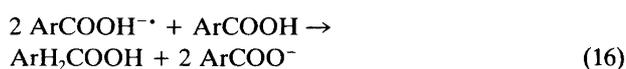
$$da/d\tau = -\lambda_2 ab \quad (12)$$

$$db/d\tau = -2\lambda_2 ab \quad (13)$$

$$dc/d\tau = 2\lambda_2 ab \quad (14)$$

$$dd/d\tau = \lambda_2 ab \quad (15)$$

The stoichiometric equation associated with the formation of the dihydrogenated products, eqns. (2)–(4), is given by eqn. (16), which gives the relationship, eqn. (17), between  $a$  and  $b$ .



$$b_m - b = 2(a_m - a) \quad (17)$$

The subscript  $m$  in eqn. (17) refers to the value of the concentration parameters *after* evaluation of the diffusion terms, but *before* evaluation of the kinetic terms. From eqn. (17) an expression for  $a$  is easily obtained, which after the introduction in eqn. (13) results in eqn. (18).

$$db/d\tau = -2\lambda_2 \left( \frac{2a_m - b_m + b}{2} \right) b \quad (18)$$

After rearrangement of eqn. (18) and integration from  $b_m$  to  $b$  and from  $\tau$  to  $\tau + \Delta\tau$  in the usual manner,<sup>20,57</sup> the expression for  $b$  given by eqn. (19) is obtained.

$$b = \frac{b_m(2a_m - b_m)}{2a_m \exp[\lambda_2 \Delta\tau(2a_m - b_m)] - b_m} \quad (19)$$

The value of  $a$  may now be obtained from eqn. (17) as  $(2a_m - b_m + b)/2$ . The values of  $c$  and  $d$  may be obtained in a similar fashion from the appropriate stoichiometric equation as  $c = b_m + c_m - b$  and  $d = (2d_m + b_m - b)/2$ , respectively.

The results of these calculations were used as input in an equilibrium treatment of reaction (6). With the same notation as before and  $e = [\text{ArH}_2\text{COO}^-]/C_{\text{ArCOOH}}^\circ$  we obtain the following expression for  $K_6$ , eqn. (20) where  $\Delta$  is the con-

$$\frac{(e + \Delta)(a + \Delta)}{(d - \Delta)(c - \Delta)} = K_6 \quad (20)$$

centration change caused by reaction (6). Rearrangement of eqn. (20) results in a second-order equation in  $\Delta$  and the analysis shows that only the positive root results in concentrations equal to or larger than zero in all volume elements. For the special case,  $K_6 = 1$ , the calculation of  $\Delta$  degenerates to eqn. (21).

$$\Delta = \frac{cd - ae}{a + c + d + e} \quad (21)$$

Calculations were carried out for pre-selected values of  $K_6$  at different values of  $\lambda_2$  in the range 0.01–100.

The two limiting cases,  $K_6 = 0$  and  $K_6 = \infty$ , were treated separately. The first case,  $K_6 = 0$ , is equivalent to a scheme including only reactions (2)–(4), and the second scheme corresponds to the inclusion of reaction (6) as a fast and irreversible process that affects only the stoichiometry of the overall reaction. At  $K_6 = 0$  the kinetic problem reduces to eqns. (12)–(13), and for  $K_6 = \infty$  only eqn. (13) has to be considered, since in this case the stoichiometry is given by eqn. (22), and accordingly,  $da/dt = 0$ . Calculations for these two cases were carried out at values of  $\lambda_2$  in the same range as before.



The simulations were carried out with double precision on an IBM desk computer, model 6151-115, equipped with an Advanced Floating Point Accelerator.

**Acknowledgements.** The Academy of Sciences of the USSR and The Danish Ministry of Education are acknowledged for their help in making visits by A.S.M. and V.P.G. to The H. C. Ørsted Institute possible. One of the authors (O.H.) gratefully acknowledges the receipt of funds from The Carlsberg Foundation and The Danish Natural Science Research Council for purchase of electrochemical instrumentation.

## References

- Amatore, C., Capobianco, G., Farnia, G., Sandonà, G., Savéant, J.-M., Severin, M. G. and Vianello, E. *J. Am. Chem. Soc.* **107** (1985) 1815, and references cited therein.
- Dal Moro, A., Farnia, G., Marcuzzi, F. and Melloni, G. *Nouv. J. Chim.* **4** (1980) 3.
- Nuntnarumit, C. and Hawley, M. D. *J. Electroanal. Chem.* **133** (1982) 57.
- Janata, J., Gendell, J., Lawton, R. G. and Mark, H. B., Jr. *J. Am. Chem. Soc.* **90** (1968) 5226.
- Jezorek, J. R., Lagu, A. L., Seigel, T. M. and Mark, H. B., Jr. *J. Org. Chem.* **38** (1973) 788.
- Leedy, D. W. and Munk, D. L. *J. Am. Chem. Soc.* **93** (1971) 4264.
- Farnia, G., Romanin, A., Capobianco, G. and Torzo, F. *J. Electroanal. Chem.* **33** (1971) 31.
- Roffia, S., Gottardi, C. and Vianello, E. *J. Electroanal. Chem.* **142** (1982) 263.
- Farnia, G., Mengoli, G. and Vianello, E. *J. Electroanal. Chem.* **50** (1974) 73.
- Farnia, G., Roque da Silva, A. and Vianello, E. *J. Electroanal. Chem.* **57** (1974) 191.
- Buchta, R. C. and Evans, D. H. *Anal. Chem.* **40** (1968) 2181.
- Buchta, R. C. and Evans, D. H. *J. Org. Chem.* **35** (1970) 2844.
- Buchta, R. C. and Evans, D. H. *J. Electrochem. Soc.* **117** (1970) 1494.
- Wawzonek, S. *J. Electrochem. Soc.* **128** (1981) 840.
- Ebersson, L. and Utley, J. H. P. In: Baizer, M. M. and Lund, H., Eds., *Organic Electrochemistry*, 2nd ed., Dekker, New York 1983, Chap. 11.
- Barradas, R. G., Kutowy, O. and Shoesmith, D. W. *Electrochim. Acta* **19** (1974) 49.
- Coetzee, J. F. and Kolthoff, I. M. *J. Am. Chem. Soc.* **79** (1957) 6110.
- Wang, H. and Hammerich, O. *Manuscript in preparation*.
- Dietz, R. In: Baizer, M. M. and Lund, H., Eds. *Organic Electrochemistry*, 2nd ed., Dekker, New York 1983, Chap. 6.
- Nielsen, M. F., Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B* **40** (1986) 101.
- Amatore, C., Gareil, M. and Savéant, J.-M. *J. Electroanal. Chem.* **147** (1983) 1.
- Nielsen, M. F., Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B* **41** (1987) 50.
- Amatore, C. and Savéant, J.-M. *J. Electroanal. Chem.* **86** (1978) 227.
- Mendkovich, A. S. and Hammerich, O. *Work in progress*.
- Jensen, B. S. and Parker, V. D. *Electrochim. Acta* **18** (1973) 665.
- Nielsen, M. F. and Hammerich, O. *Acta Chem. Scand., Ser. B* **41** (1987) 668.
- Svanholm, U., Hammerich, O. and Parker, V. D. *J. Am. Chem. Soc.* **97** (1975) 101.
- Discussions at the 15th Sandbjerg Meeting on Organic Electrochemistry, June 1990, where this work was presented in part.
- Kolthoff, I. M. and Reddy, T. B. *J. Electrochem. Soc.* **108** (1961) 980.
- Cofré, P. and Sawyer, D. T. *Anal. Chem.* **58** (1986) 1057.
- Simic, M. and Hoffman, M. Z. *J. Phys. Chem.* **76** (1972) 1398.
- Neta, P. and Fessenden, R. W. *J. Phys. Chem.* **77** (1973) 620.
- Buick, A. R., Kemp, T. J., Neal, G. T. and Stone, T. J. *J. Chem. Soc.* (1970) 2227.
- Zuman, P. *Substituent Effects in Organic Polarography*, Plenum Press, New York 1967.
- Coleman, J. P. In: Patai, S., Ed., *The Chemistry of Acid Derivatives*, Suppl. B, Wiley-Interscience, New York 1979, p. 782.
- Mendkovich, A. S. and Hammerich, O. *Unpublished results*.
- De Luca, C., Giomini, C. and Rampazzo, L. *J. Electroanal. Chem.* **207** (1986) 161.
- Hirayama, M. *Bull. Chem. Soc. Jpn.* **40** (1967) 1822.
- Il'yasov, A. V., Kargin, Yu. M., Levin, Ya. A., Morozova, I. D. and Sotnikova, N. N. *Dokl. Akad. Nauk SSSR* **179** (1968) 1141.
- Il'yasov, A. V., Kargin, Yu. M., Levin, Ya. A., Morozova, I. D. and Sotnikova, N. N. *Izv. Akad. Nauk SSSR Ser. Khim.* **5** (1968) 1030.
- Mendkovich, A. S. and Gulyai, V. P. *The Theoretical Basis of the Chemistry of Organic Anion Radicals*, Nauka Publ., Moscow 1990.
- Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B* **37** (1983) 379 and references cited therein.
- Nadjo, L. and Savéant, J.-M. *J. Electroanal. Chem.* **48** (1973) 113.
- Hammerich, O. and Parker, V. D. In: Lund, H. and Baizer, M. M., Eds., *Organic Electrochemistry*, 3rd ed., Dekker, New York 1991, Chap. 3.
- Parker, V. D. *Acta Chem. Scand.* **24** (1970) 2768.
- Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem.* **121** (1981) 73.
- Parker, V. D. *Electroanal. Chem.* **14** (1986) 1.
- Kortüm, G., Vogel, W. and Andrussov, K., Eds., IUPAC, *Dissociation Constants of Organic Acids in Aqueous Solution*, Butterworths, London 1961.
- Amatore, C. and Savéant, J.-M. *J. Electroanal. Chem.* **107** (1980) 353.
- Kvalvåg, E. and Hammerich, O. *To be published*.
- Klopman, G., Ed., *Chemical Reactivity and Reaction Paths*, Wiley, New York 1974.

52. Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D. and Mallard, W. G. *J. Phys. Chem. Ref. Data* 17, *Suppl. 1* (1988) 746, 755.
53. Mendkovich, A. S., Hammerich, O., Nielsen, M. F. and Ruskov, A. I. *To be published*.
54. Gross, H., Rusche, J. and Mirsch, M. *Chem. Ber.* 96 (1963) 1382.
55. Marshall, J. L. and Folsom, T. K. *J. Org. Chem.* 36 (1971) 2011.
56. Feldberg, S. W. *Electroanal. Chem.* 3 (1969) 199.
57. Nielsen, M. F., Almdal, K., Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. A* 41 (1987) 423.

Received December 4, 1990.