

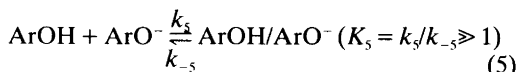
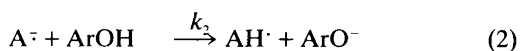
## The Stoichiometric Consequences of Intramolecular or Ion Pair Stabilization of the Anions Formed During Protonation of Anion Radicals in Aprotic Solvents

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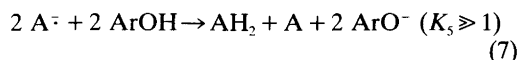
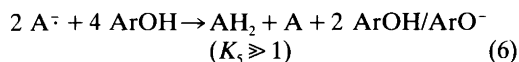
Nielsen, M. F., Hammerich, O. and Parker, V. D., 1987. The Stoichiometric Consequences of Intramolecular or Ion Pair Stabilization of the Anions Formed During Protonation of Anion Radicals in Aprotic Solvents. – Acta Chem. Scand. B 41: 64–66.

The mechanism of protonation of anion radicals derived from alternant aromatic hydrocarbons ( $A^{\cdot-}$ ) by simple phenols ( $ArOH$ ) in polar, aprotic solvents includes the reaction sequence given by eqns. (1)–(5) as the essential steps.<sup>1–10</sup> Studies of the kinetics



of these reactions by transient electroanalytical techniques like double potential step chronoamperometry (DPSC) and derivative cyclic voltammetry (DCV) have in general been conducted under conditions which were believed to ensure that the data analysis could be carried out under pseudo first-order conditions. These conditions have typically involved concentrations in the ranges  $C_A^\circ = 0.5 - 2$  mM and  $C_{ArOH}^\circ = 10 - 100$  mM. However, during recent studies of the protonation of the anthracene anion radical ( $AN^{\cdot-}$ )

by phenol ( $PhOH$ ) we have demonstrated that this excess of  $ArOH$  over  $A$  is not sufficiently large to allow the neglect of  $ArOH$  consumed during the reaction.<sup>9,10</sup> The deviations from pseudo first-order conditions are accentuated by the formation of so-called homoconjugated complexes between  $ArOH$  and  $ArO^-$ , which due to the high equilibrium constant for their formation<sup>11–17</sup>,  $K_5 \geq 10^3$  M<sup>-1</sup>, results in the consumption of four rather than two molecules of  $ArOH$  within the time scale of the experiment, as shown in eqns. (6) and (7).



The fact that convenient concentration ranges do not ensure pseudo first-order conditions stimulated attempts to study the protonation of  $AN^{\cdot-}$  by  $PhOH$  under conventional second-order conditions, *i.e.* where  $C_{AN}^\circ \approx C_{PhOH}^\circ$ .<sup>10</sup> One interesting aspect of this approach is that the stoichiometry of the process could be evaluated by comparison of experimental DCV data with working curves calculated for the two limiting cases: (a) mechanism (1)–(4), stoichiometry (7), and (b) mecha-

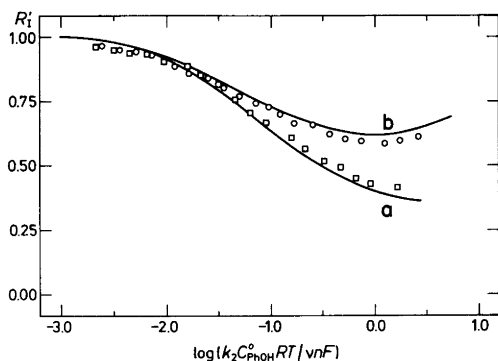
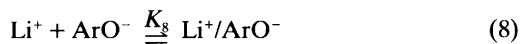


Fig. 1. Derivative cyclic voltammetry data for  $C_{\text{PhOH}}^{\circ} = C_{\text{AN}}^{\circ} = 2 \text{ mM}$  in the absence (circles) and the presence (squares) of  $\text{LiClO}_4$  (25 mM) at  $22^{\circ}\text{C}$ . The working curves (full lines) are for (a) mechanism (1)–(4) and (b) mechanism (1)–(4) plus irreversible (5), at  $C_{\text{PhOH}}^{\circ}/C_{\text{AN}}^{\circ} = 1$ .

nism (1)–(4) plus irreversible (5), stoichiometry (6). As an example, experimental DCV data obtained with *N,N*-dimethylformamide (DMF) as solvent at  $C_{\text{AN}}^{\circ} = C_{\text{PhOH}}^{\circ} = 2 \text{ mM}$  are shown in Fig. 1 (circles) and it is clearly seen that the experimental data follow closely working curve (b), indicating that (5) may indeed be treated as an irreversible process and that protonation of  $\text{AN}^{\cdot-}$  by  $\text{PhOH}/\text{PhO}^-$  does not interfere kinetically under the conditions of the experiment.

The major cause of the high values of  $K_5$  in polar aprotic solvents is the poor ability of these solvents to effectively solvate anions.<sup>18</sup> This problem might be partly overcome by employing phenols for which the anions are stabilized by intramolecular formation of hydrogen bonds to the negatively charged oxygen atoms. Two likely candidates are 2-hydroxybenzyl alcohol (HBA) and 1,2-dihydroxybenzene (DHB). Another approach would be to stabilize the phenolate ions by ion pairing with e.g. lithium ions (eqn. 8).



The value of  $K_8$  for  $\text{Ar} = 2\text{-methoxyphenyl}$  has recently been estimated to be of the order of  $2 \cdot 10^4 \text{ M}^{-1}$  in DMF<sup>19</sup> and is expected to be considerable also for  $\text{Ar} = \text{Ph}$ . The stabilization of  $\text{ArO}^-$  in either way will result in a reduced demand for additional  $\text{ArOH}$ ; consequently, it is expected that the experimental points when plot-

ted as  $R'_i$ , the derivative peak current ratio, vs.  $\log(k_2 C_{\text{ArOH}}^{\circ} RT / v n F)$  will approach working curve (a) for the conventional stoichiometry (7). This is, in fact, what is observed.

Fig. 1 shows the experimental data obtained for the solution which was 2 mM in both AN and PhOH before (circles) and after (squares) the addition of  $\text{LiClO}_4$  (25 mM). The shift from stoichiometry (6) to stoichiometry (7) is evident and demonstrates that  $\text{Li}^+$  ions very effectively eliminate the need for stabilization of  $\text{PhO}^-$  via the formation of the homoconjugated complex,  $\text{PhOH}/\text{PhO}^-$ .

The intramolecular stabilization caused by the presence of the hydroxymethyl group (HBA) or the additional hydroxy group (DHB) was less effective. Under similar conditions, i.e.  $C_{\text{ArOH}}^{\circ} = C_{\text{AN}}^{\circ} = 2 \text{ mM}$ , the use of these two phenols resulted in the experimental data given in Fig. 2 (HBA, circles and DHB, squares). In both cases the experimental points are shifted towards working curve (a) when compared to the results for PhOH, but the position of the data points shows that the magnitudes of  $k_5$  and  $K_5$  are not sufficiently small to allow complete neglect of the formation of the  $\text{ArOH}/\text{ArO}^-$  complex.

A 2-hydroxymethyl group appears to be more effective than a 2-hydroxy group in terms of stabilizing the corresponding phenolate ion under the present conditions. This is in keeping with the general observation that the strength of intramolecular hydrogen bonds is greater in six-mem-

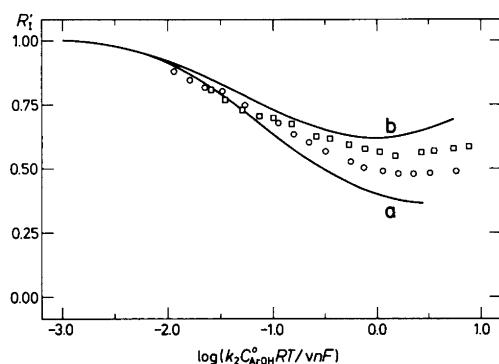


Fig. 2. Derivative cyclic voltammetry data for  $C_{\text{HBA}}^{\circ} = C_{\text{AN}}^{\circ} = 2 \text{ mM}$  (circles) and  $C_{\text{DHB}}^{\circ} = C_{\text{AN}}^{\circ} = 2 \text{ mM}$  (squares) at  $22^{\circ}\text{C}$ . The working curves (full lines) are for (a) mechanism (1)–(4) and (b) mechanism (1)–(4) plus irreversible (5), at  $C_{\text{ArOH}}^{\circ}/C_{\text{AN}}^{\circ} = 1$ .

bered rings (the anion of HBA) than in five-membered rings (the anion of DHB).<sup>20-21</sup>

Since working curves were not available for intermediate values of  $K_5$ , it was decided to estimate the second-order rate constants,  $k_2$ , from the corresponding  $v_{1/2}$  values obtained at  $C_{\text{ArOH}}/C_{\text{AN}} = 10$  and  $C_{\text{AN}} = 1$  mM assuming pseudo first-order conditions. The latter concentration ratio was chosen as a compromise between the need to keep the sweep rate in the measurable range and the wish to reduce the error in  $k_2$  caused by not taking the consumption of PhOH into account in the calculation.<sup>10</sup> The values of  $k_2$  obtained in this way were the following at 22 °C:  $k_2(\text{PhOH}) = 4600 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_2(\text{PhOH}, \text{Li}^+ [25 \text{ mM}]) = 5800 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_2(\text{HBA}) = 16000 \text{ M}^{-1}\text{s}^{-1}$  and  $k_2(\text{DHB}) = 85000 \text{ M}^{-1}\text{s}^{-1}$ . A discussion of the relation between the structure of ArOH and the magnitude of  $k_2$  is beyond the scope of this communication, but it is of interest to note the moderate increase in  $k_2$  caused by the presence of  $\text{Li}^+$  ions. We believe that this rate enhancement is most likely due to the presence of  $\text{Li}^+/\text{PhOH}$  complexes in the aprotic solvent. The equilibrium acidity of  $\text{Li}^+/\text{PhOH}$  in DMF is not known, but the complex is believed to be a much stronger acid than free phenol, partly as a consequence of the high value of  $K_8$ . Ion pairs between  $\text{AN}^-$  and  $\text{Li}^+$  are of only minor importance in DMF<sup>22</sup> and are not expected to contribute to the magnitude of  $k_2(\text{PhOH}/\text{Li}^+ [25 \text{ mM}])$ .

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