

## Short Communications

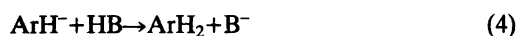
### The Competition between Proton and Electron Transfer during the Reaction of Anthracene Anion Radical with Water or Alcohols in Aprotic Media.

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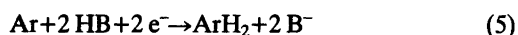
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The reaction of anion radicals derived from polycyclic aromatic hydrocarbons ( $\text{Ar}^{\cdot-}$ ) with weak acids (HB) like  $\text{H}_2\text{O}$ , alcohols (ROH) or phenol (PhOH) in aprotic media was for a long time believed to be adequately described by eqns. (1)–(4) or (2)–(4).<sup>1–4</sup> The first sequence, the  $\text{ECE}_h$ -mechanism, pertains to voltammetric conditions and the second, the half-regeneration scheme, is related to homogeneous solutions, *i.e.* in the absence of an additional electron source. This difference in



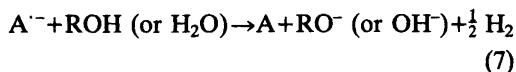
conditions affects the stoichiometry of the two schemes, which are summarized in eqns. (5) and (6), respectively. In the first case Ar may in principle be converted quantitatively to  $\text{ArH}_2$ , while in the second the maximum possible yield of  $\text{ArH}_2$  is limited to 50 %.



The reaction between anthracene anion radical ( $\text{A}^{\cdot-}$ ) and  $\text{H}_2\text{O}$  or PhOH in DMF has served as a popular model system for kinetic studies of the process.<sup>5–16</sup> When the decay of  $\text{A}^{\cdot-}$  in the presence of  $\text{H}_2\text{O}$  was monitored by e.s.r.<sup>5–6</sup> or visible spectroscopy<sup>7–9</sup> results were obtained, which were interpreted in favor of mechanism (2)–(4) with step (2) being rate determining. The same conclusion regarding the rate determining step was arrived at as a result of electrochemical studies of A in the presence of PhOH.<sup>10–11</sup> However, the application of newly developed voltammetric techniques has indicated that the reaction of  $\text{A}^{\cdot-}$  and PhOH is kinetically more complicated<sup>12–14</sup> and recent work<sup>15</sup> has unambiguously demonstrated that the reverse reaction of (2) may manifest itself kinetically. Therefore, obviously, (2) is also reversible when less acidic hydroxy compounds like  $\text{H}_2\text{O}$  are employed.

The kinetic studies referred to above were all carried out under the tacit assumption that the stoichiometry of the reactions is indeed satisfactorily described by eqns. (5) and (6). The purpose of the present note is to draw the attention to the fact that this is generally not the case in DMF and DMSO for very weak acids like  $\text{H}_2\text{O}$  and ROH.

The course of the reaction was studied by preparative cathodic reduction of A in the presence of  $\text{H}_2\text{O}$ , ROH or PhOH at constant current,<sup>16</sup> (25 mA), in a divided cell allowing an amount of charge equivalent to 2 F/mol to pass the solution. The concentrations of A and 9,10-dihydroanthracene ( $\text{AH}_2$ ) during the reduction and the stoichiometry after reduction were monitored by glc analysis. The rate of conversion of A to  $\text{AH}_2$  as well as the relative yields of A and  $\text{AH}_2$  given in Table 1 were found only to be in agreement with (5) when the acid was PhOH or  $\text{H}_2\text{O}/\text{Li}^+$  (0.1 M). In all other cases regeneration of A has taken place in a competing reaction, which most likely involves electron transfer from  $\text{A}^{\cdot-}$  to  $\text{H}_2\text{O}$  or ROH. However, the formation of  $\text{H}_2$  according to (7) could not be detected, but GLC analysis of the



**Table 1.** Derivative cyclic voltammetric data and relative yields of anthracene (A) and 9,10-dihydroanthracene (AH<sub>2</sub>) after cathodic reduction of A in DMF and DMSO containing hydroxy compounds.

ROH	pK <sub>a</sub> (H <sub>2</sub> O)	pK <sub>a</sub> <sup>o</sup> (DMSO)	A (%) <sup>b</sup> (DMSO)	AH <sub>2</sub> (%) <sup>b</sup>	A (%) <sup>b</sup> (DMF)	AH <sub>2</sub> (%) <sup>b</sup>	v <sub>0.8</sub> /V · s <sup>-1</sup> (DMF)
<i>t</i> -BuOH	18	32.2	43	57	100	0	0.02
H <sub>2</sub> O	15.7	31.4	53	47	98	2	0.031
H <sub>2</sub> O/Li <sup>+</sup> (0.1)	—	—	—	—	0	100	— <sup>d</sup>
<i>i</i> -PrOH	16	30.2	49	51	93	7	0.18
EtOH	15.8	29.8	44	56	65	35	4.78
MeOH	15.1	29.0	35	65	58	42	25.2
HOCH <sub>2</sub> CH <sub>2</sub> OH	15.1	—	34	66	14	86	315
PhOH	10	25.3	4	96	2	98	— <sup>d</sup>

<sup>a</sup> From Ref. 25. <sup>b</sup> After the passage of 2 F/mol. The cathode was a mercury pool and the supporting electrolyte was Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M). C<sub>ROH</sub>=C<sub>H<sub>2</sub>O</sub>=0.5 M. C<sub>PhOH</sub>=20 mM. C<sub>A</sub>=2 mM. <sup>c</sup> The voltage sweep rate necessary for the derivative peak ratio to equal 0.8. C<sub>ROH</sub>=C<sub>H<sub>2</sub>O</sub>=3.6 M. <sup>d</sup> Too fast to measure.

product mixture obtained when a solution of A<sup>-</sup> in DMSO, prepared electrochemically, was treated with an excess of EtOH, demonstrated the presence of products more volatile than EtOH. We suspect these to arise from reaction of H<sup>+</sup> with the solution components.

The kinetics of the reaction in DMF were studied by derivative cyclic voltammetry.<sup>12,17</sup> The relative over-all rates, represented by v<sub>0.8</sub>, are likewise summarized in Table 1. The v<sub>0.8</sub> values refer to the voltage sweep rates necessary for the derivative peak ratios to equal 0.8. The most prominent feature of the rate data is that the significant increase in v<sub>0.8</sub> in going from EtOH to HOCH<sub>2</sub>CH<sub>2</sub>OH, which amounts to almost two orders of magnitude, is only accompanied by an increase in the product ratio, AH<sub>2</sub>/A, from 35/65 to 86/14, approximately a factor of ten. Thus, the kinetic data indicate that the rate of the competing reaction depends on structural changes of the hydroxy compounds in a manner resembling that of proton transfer, which further supports the suggestion that this reaction is indeed electron transfer from A<sup>-</sup> to H<sub>2</sub>O or ROH. The transition states for proton and electron transfer are both expected to involve considerable stretching of the O-H bond together with the development of negative charge on the oxygen atom, and thus to respond similarly on structural changes.

The relative product yields seem to indicate that the AH<sub>2</sub>/A ratio increases with increasing acidity of ROH although the comparison is made difficult by the apparent lack of a consistent set of pK<sub>a</sub> data for aliphatic alcohols in DMF. The trend appears to be less conspicuous in DMSO than in DMF. This effect is also illustrated by the result of addition of Li<sup>+</sup>-ions to DMF containing

H<sub>2</sub>O, which causes the yield of AH<sub>2</sub> to increase from 2 to 100%. On top of the enlarged acidity of H<sub>2</sub>O caused by Li<sup>+</sup> due to complex formation, Li<sup>+</sup>-ions do also favor the formation of AH<sub>2</sub> through strong association with OH<sup>-</sup>.<sup>18</sup> As a result of this, the proton transfer reaction becomes effectively irreversible and prevents A<sup>-</sup>, once protonated, to escape *via* the competing electron transfer.

That protonation of anion radicals by H<sub>2</sub>O or ROH may be accompanied by competing electron transfer has recently been the subject of a vigorous discussion.<sup>19-23</sup> When crystalline sodium naphthalenide (Na<sup>+</sup>,N<sup>-</sup>) was treated with H<sub>2</sub>O evolution of H<sub>2</sub> was observed, which was attributed to reduction of H<sub>2</sub>O by N<sup>-</sup>.<sup>19</sup> This interpretation was strongly criticized,<sup>20</sup> but later work<sup>21-23</sup> seems to have confirmed the original interpretation. In contrast, protonation was the only reaction observed for Na<sup>+</sup>,A<sup>-</sup>. This difference in behavior between free A<sup>-</sup>, as in DMSO or DMF, and A<sup>-</sup> associated with alkali metal ions may well be connected with the common observation that free Ar<sup>-</sup> ions are stronger reducing agents than, *e.g.*, Na<sup>+</sup>,Ar<sup>-</sup>. Detailed studies are in progress on these and related systems.

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