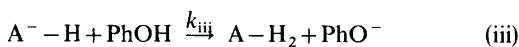
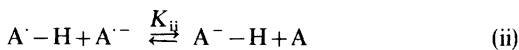
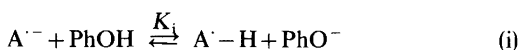


The Kinetics and Mechanism of the Protonation of 9-Phenyl- and 9,10-Diphenylanthracene Anion Radicals by Phenol

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At low substrate and phenol concentrations the anion radicals of 9-phenyl- and 9,10-diphenylanthracene undergo protonation by a multi-step mechanism with reaction orders in both anion radical and phenol approaching 2. The reaction orders decrease with increasing substrate and phenol concentrations approaching limiting values of 1. The kinetics of the reactions were analyzed using linear sweep voltammetry and derivative cyclic voltammetry. The data are most consistent with mechanism (i–iii) and the relative importance of the

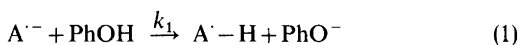


various steps in determining the rate is concentration dependent. It is concluded that the 9,10-diphenylanthracene ion radicals, both anion and cation, undergo reactions following mechanisms of great complexity and these systems are not suitable as models.

The protonation of the anthracene anion radical by phenol has recently been shown to be more complex than previously supposed.¹ The protonation of aromatic hydrocarbon anion radicals, in general, is commonly considered to be a well-behaved process of the ECE type where the rate determining step is the reaction of the anion radical with the proton donor.^{2,3} It has been suggested³ that the protonation of 9,10-diphenylanthracene (DPA) anion radical, as reported by Santhanam and

Bard,⁴ should serve as a model of the ECE behaviour.

An important consideration regarding multi-step processes of this type is the meaning of kinetic parameters measured for the systems. For example, rate constants for the protonation of a large number of hydrocarbon anion radicals were assigned assuming that the values refer to the microscopic kinetics of reaction (1).³ When this is the case, a



study of such systems represents a means of obtaining valuable mechanistic information especially pertaining to structure-reactivity and activation parameters. However, if the assumption of the ECE behaviour is not well-grounded and subsequent reaction steps influence the kinetics of the reactions, the mechanistic and reactivity conclusions will be of little value.

Since the study of anthracene anion radical protonation revealed a very complex kinetic situation, it is of importance to determine whether the complex mechanism in that case is generally followed or if it is exceptional. Because the DPA-phenol system in DMF has been suggested as a model for the study of such reactions it was selected for further study together with the 9-phenylanthracene (PA)-phenol system. Conclusions from this study, along with those from the anthracene work, can be expected to be generally valid for aromatic hydrocarbon anion radicals in polar aprotic solvents.

RESULTS

Kinetic measurements. The rate of protonation of DPA^- by phenol was low enough to preclude the use of linear sweep voltammetry (LSV). Measurements in this case were made by derivative cyclic voltammetry (DSV)^{5,6} using the analysis procedure recently presented.⁷ The method consists of measuring $v_{1/2}$ the voltage sweep rate when R_f equals 0.500. R_f is the ratio of the derivative peak heights on the backward and forward scans of a cyclic voltammogram. The apparent rate constant for the reaction following charge transfer, k_{app} , is directly proportional to $v_{1/2}$. Both LSV and DCV analyses were applied to the protonation reactions of PA^- . The LSV analysis consists of measuring the peak potential dependence on the voltage sweep rate (2), the substrate concentration (3) and an additional reactant (4).⁸ The constants,

$$dE^p/d \log v = 1/(b+1) \ln 10 RT/F \quad (2)$$

$$dE^p/d \log C_A = (a+b+i-1)/(b+1) \ln 10 RT/F \quad (3)$$

$$dE^p/d \log C_X = x/(b+1) \ln 10 RT/F \quad (4)$$

a , b , i and x are the reaction orders in the various species where A is the substrate, B the product of electron transfer, I is formed during the process and further participates. The rate law can then be derived directly from equations (2–4) in the form

$$\text{Rate} = k_{app} C_A^a C_B^b C_I^i C_X^x \quad (5)$$

of (5). In this study, X refers to PhOH and I to PhO^- .

The protonation of DPA^- . A series of experiments was carried out in DMF containing Bu_4NBF_4

Table 1. A comparison of the kinetics of the protonation of 9,10-diphenylanthracene anion radical by phenol in buffered and unbuffered DMF.^a

[DPA]/mM	$v_{1/2}$ (unbuffered)/ $V s^{-1}$	$v_{1/2}$ (buffered)/ $V s^{-1}$
0.20	0.34	0.87
0.40	0.86	0.76
0.80	1.49	0.41
1.60	1.52	0.44

^a The unbuffered solution contained phenol (100 mM) while the buffered solution contained phenoxide ion (100 mM) as well. Supporting electrolyte was Bu_4NBF_4 (0.1 M).

Table 2. Dependence of the rate of protonation of DPA^- anion radical on the substrate, phenol and phenoxide ion concentrations.^a

([PhOH]/[PhO ⁻])/ (mM/mM)	[DPA]/mM	$v_{1/2}/V s^{-1}$
50/100	1.0	0.29
100/100	1.0	0.88
200/100	1.0	2.40
200/100	2.0	1.95
200/100	4.0	1.56
100/20	1.0	3.30
100/50	1.0	1.42
100/100	1.0	0.88

^a In DMF containing Bu_4N^+ (0.1 M) at 22 °C.

(0.1 M) on the protonation of DPA^- by phenol in both unbuffered and buffered solution. The buffered solution contained PhO^- (100 mM) prepared *in situ* by the addition of Bu_4NOH . The results of DCV kinetics on these solutions where the DPA concentration was varied from 0.20 to 1.60 mM are summarized in Table 1. The features of interest in the data are that k_{app} ($\sim v_{1/2}$) increases significantly with increasing concentration in unbuffered solution while the opposite trend is observed in buffered media. A qualitative interpretation of the data is that the reaction order in DPA^- is greater than unity and the reaction is inhibited by PhO^- .

The data in Table 2, all from measurements in buffered solution, were obtained to determine the reaction orders in DPA^- , DPA , PhOH and PhO^- . The first three entries show that when only the PhOH concentration is varied ($[\text{PhO}^-] = 100 \text{ mM}$), $v_{1/2}$ increases by very nearly a factor of three for a two-fold increase in $[\text{PhOH}]$. Doubling the DPA concentration was accompanied by a 20 % decrease in $v_{1/2}$ while a greater inhibiting effect was observed with increasing concentration of PhO^- . The reaction orders can be derived from eqns. (6) and (7).⁷

$$R_{A/B} = 1 + z, (v_{1/2}/C_A^z = \text{constant}) \quad (6)$$

$$R_{(\text{PhOH or PhO}^-)} = x, (v_{1/2}/C_{(\text{PhOH or PhO}^-)}^x = \text{constant}) \quad (7)$$

The order with respect to DPA^- and DPA can only be obtained as the combination of the two, $R_{A/B}$, from (6). This is the distinct advantage of LSV over other electrode kinetic techniques in that the orders are separable as in (3) and (4). The

Table 3. Summary of linear sweep voltammetry data for the reduction of 9-phenylanthracene in DMF in the presence of phenol.^a

[PA]/mM	dE ^p /d log ν		dE ^p /d log C _{PhOH}
	20 mM [PhOH]	200 mM [PhOH]	
0.2	22.8	23.0	27.6
0.4	21.8	24.8	31.8
0.8	22.7	26.7	32.7
1.6	22.5	29.9	31.9

^a The slopes are in mV/decade.

apparent reaction orders that can be derived from the data in Table 2 are, R_{DPA/DPA^{•-}} = 0.7 R_{PhOH} = 1.6 R_{PhO⁻} ~ 0.8.

The protonation of PA^{•-}. A summary of LSV kinetic studies on the reactions of PA^{•-} with PhOH in DMF containing Bu₄NBF₄ (0.1 M) can be found in Table 3. Each of the values of dE^p/d log ν were based on measurements at 100, 200, 400 and 1,000 mV s⁻¹ with five replicates at each sweep rate. At a phenol concentration of 20 mM, dE^p/d log ν was independent of [PA] and was equal to 22.5(±0.5) mV/decade. At [PhOH] equal to 200 mM, dE^p/d log ν increased from 23.0 to 29.9 mV/decade as [PA] was increased from 0.2 to 1.6 mM. These results indicate that at the lower phenol concentration, R_{PA^{•-}} is very close to 2 but decreases to 1 at the highest phenol and PA concentrations. These conclusions follow from eqn. (2). It is not possible to estimate values of R_{PhOH} from the data

Table 4. Kinetic data for the protonation of 9-phenylanthracene anion radical in buffered and unbuffered DMF.^a

([PhOH]/[PhO ⁻])/ (mM/mM)	[PA]/mM	v _{1/2} /V s ⁻¹
100/0	0.3	68.4
100/0	0.4	41.9
100/0	0.8	38.1
100/0	1.8	31.7
50/0	1.0	18.0
100/0	1.0	29.6
200/0	1.0	67.9
100/100	0.2	39.0
100/100	0.4	33.7
100/100	1.0	27.4

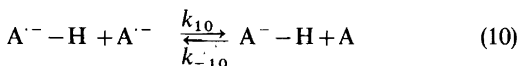
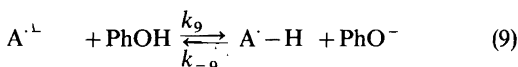
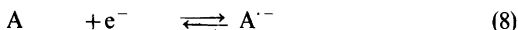
^a In solvent containing Bu₄NBF₄ (0.1 M) at 22 °C.

since (4) is based on the assumption that *b*, which is R_{PA^{•-}} in this case, is a constant. Since the latter is dependent on [PhOH], (4) does not apply. However, at all [PA] dE^p/d log C_{PhOH} is greater than dE^p/d log ν at either phenol concentration. This can only be interpreted to indicate that R_{PhOH} is greater than 1.

Derivative cyclic voltammetry kinetic data for the protonation of PA^{•-} in buffered and unbuffered DMF are summarized in Table 4. In this case, v_{1/2} decreases with increasing substrate concentration in unbuffered solution indicating the importance of inhibition by PhO⁻. The latter is also evident from consideration of the first four entries in the table as compared to the last three. In all cases v_{1/2} was lower in the presence of PhO⁻. A nearly first order dependence on [PhOH] was observed in unbuffered solution.

DISCUSSION

A feature common to all of the kinetic analyses of the data for the protonation of DPA^{•-} and PA^{•-} by phenol is the obvious complexity of the reactions. In no case do integral reaction orders appear to be involved. For both DPA^{•-} and PA^{•-} reactions, the order in phenol appears to be greater than 1. Since the products of these reactions are dihydro derivatives,³ account must be taken of the addition of the second proton in formulating a rate law. Thus, the overall reaction scheme must include steps (8)–(11). This reaction scheme has two



reactive intermediates, A^{•-}H and A^{•-}H, which are expected to be present in only very low concentrations. Thus, if the steady state assumption is made for [A^{•-}H], it is necessary to assume equilibrium for reaction (9) in order to obtain a workable rate equation. Doing this, we arrive at rate law (12). This rate law has the general features

$$\text{Rate} = \frac{k_{10}k_{11}K_9[A^{\cdot-}]^2[\text{PhOH}]^2}{(k_{-10}[A] + k_{11}[\text{PhOH}])(\text{PhO}^-)} \quad (12)$$

necessary to explain the kinetic data. Simplification can lead to integral reaction orders in all entities in the rate expression. Limiting orders of 2 are predicted for both $A^{\cdot-}$ and PhOH and limiting inverse 1 orders in A and PhO^- are possible if $k_{11}[\text{PhOH}] \gg k_{-10}[A]$. On the other hand if this simplification is not valid, non-integral reaction orders are predicted for A, PhOH and PhO^- .

The pertinent conclusions from the data (Tables 1–4) are (i) the reaction order in $A^{\cdot-}$ varies depending upon the conditions but is always greater than 1 but less than 2, (ii) the reaction order in phenol varies between 1 and 2, (iii) inhibition is observed by both A and PhO^- and the reaction orders in some cases appear to approach -1 . On the basis of these observations, it appears that reaction scheme (8)–(11) is a reasonably good description of the mechanism. On the other hand, the assumption of equilibrium for reaction (9), necessary to arrive at rate equation (12) is probably not justified under all conditions of this study.

Further detailed analysis of the data in terms of the postulated mechanism would not appear to be productive. The most obvious, and also important, point is that the protonation of $\text{DPA}^{\cdot-}$ by phenol is not a model ECE reaction⁴ as proposed earlier.³ The protonation of $\text{DPA}^{\cdot-}$, $\text{PA}^{\cdot-}$ and anthracene anion radical¹ by phenol in DMF follow complex mechanisms of the general form of (8)–(11) and caution must be taken before making any conclusions based on kinetic data regarding the microscopic parameters for any one reaction step.

It is of interest to compare rate constants for the protonation of the three anion radicals measured under similar conditions. At $[\text{PhOH}]$ and $[\text{PhO}^-]$ in DMF equal to 100 mM, $v_{1/2}$ was observed to be 0.88 for $\text{DPA}^{\cdot-}$ and 27.4 for $\text{PA}^{\cdot-}$ at a substrate concentration of 1.0 mM. Extrapolation of the data in Ref. 1 to the same conditions results in $v_{1/2}$ equal to about 40. A reasonable explanation of this order of reactivity is that it is a reflection of the relative positions of equilibrium (9). The lower rate for $\text{DPA}^{\cdot-}$ can be due to steric effects on protonation at the 9-position or a consequence of the lower $\text{p}K_a$ of the proton adduct. The fact that the observed rates for $\text{PA}^{\cdot-}$ and anthracene anion radical are similar with the former being somewhat smaller suggests the difference to arise from the statistical factor of two equivalent positions in the anthracene

case [(9) and (10)] with only one unblocked position in $\text{PA}^{\cdot-}$.

The protonation of the substituted anthracene anion radicals is mirrored by a very similar situation in the pyridination of anthracene and 9,10-substituted anthracene cation radicals.⁹ The latter reactions have been the subject of much discussion^{9–16} and were believed, for a long time, to be a model for the ECE type behaviour of cation radicals. It now appears that the 9,10-diphenylanthracene ion radical reactions, rather than representing oversimplified reaction mechanisms, are among the most complex that have been studied. The work presented here surely supports the most recent conclusions on the $\text{DPA}^{\cdot+}$ -pyridine reaction mechanism⁹ and also adds detail that cannot be obtained in the latter system. That is, the effect of phenoxide ion on the rate of the protonation reaction does not have a counterpart in the cation radical reactions.

The protonation of aromatic hydrocarbon anion radicals and dianions have been the subject of many investigations. Most of the non-electrochemical work has been carried out in relatively non-polar etheral solvents in which ion pairs play an important role in the reactions. Much of the latter work has been reviewed by Szwarc, Streitwieser and Mowery.¹⁷

In conclusion, attention is drawn to the fact that mechanisms of the type represented by eqns. (8)–(11) are totally intractable using conventional electrode kinetic analysis with working curves based upon theoretical models. Calculations cannot be carried out for such complicated reaction schemes. The new reaction order approaches^{7,8} which do not rely on theoretical calculations show their true power in such situations.

EXPERIMENTAL

Solvent and electrolyte purification as well as the instrumentation, electrodes, cells and data handling procedures were the same as recently described.⁹ Details of the kinetic analysis methods have been presented.^{7,8} The buffers were prepared by adding the appropriate amounts of a Bu_4NOH solution in methanol (25%), Fluka, to the phenolic DMF solutions.

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