

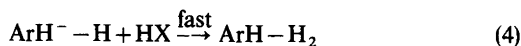
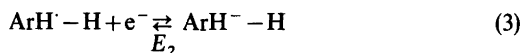
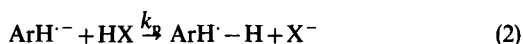
# The Mechanism of the Protonation of Anthracene Anion Radical by Phenols. The Failure of a Search for a Simple Reaction Mechanism of Ion Radicals

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The kinetics and mechanism of the protonation of anthracene anion radical in DMF by phenol or 2,6-dialkylphenols were studied. In all cases, a very complex mechanism is involved. The reactions are inhibited by phenoxide ion indicating that the initial protonation step is reversible. Depending upon both the substrate and the proton donor concentrations, the order in anion radical can vary from 1 to 2. Very close correspondence was found by two independent techniques, linear sweep voltammetry and derivative cyclic voltammetry. The mechanism consists of (a) proton transfer equilibrium, (b) electron transfer equilibrium in which the neutral radical formed in (a) is reduced to the carbanion and finally (c) the protonation of the carbanion. All three of the reactions can contribute to the overall rate of the reaction. Linear Arrhenius plots were obtained over a 40 K temperature range when the proton donor was phenol, 2,6-dimethylphenol or 2,6-di-*tert*-butylphenol. The observed activation energies are suggested to arise primarily from the protonation step.

The reduction of aromatic compounds in the presence of proton donors has received a great deal of attention. The general conclusions from a large number of such investigations were summarized by Fry and Schuettner in 1974.<sup>1</sup> The reactions were believed to pass through the "ECE" scheme (eqns. 1–4) where the second electron transfer step



$E_2$  takes place at a potential less negative than  $E_1$ . The most frequent method to analyze these protonation reactions has been using polarography where the increase in the height of the wave at the potential of the first charge transfer is used as a measure of the rate of reaction (2). The reduction of 9,10-diphenylanthracene in DMF containing phenol<sup>2</sup> was suggested as a model for the study of reactions of this type.<sup>1</sup>

There is an obvious pitfall in such studies. That is, the mechanism of the reaction must first be assumed and then the rate constants are determined by theoretical relationships based on the assumed model. The observed rate constants can vary significantly, depending upon the model used in the calculations<sup>3,4</sup>, by more than a factor of  $10^2$ .<sup>1</sup> An even more serious objection is that the mechanism should be firmly established before trying to assign rate constants to any individual steps. If the mechanism is more complex than assumed, the numerical values of rate constants are quite meaningless.

A reaction typical of those discussed above has recently been treated in more detail. The reduction of anthracene in DMF in the presence of phenol was studied by double potential step chronoamperometry by Amatore and Savéant.<sup>5</sup> The objective of the latter study was to show that the simple ECE scheme is not followed but rather the  $\text{ECE}_n$ , where the  $E_n$  means that the second electron transfer occurs

in solution as in eqn. (5), as had earlier been suggested by Hawley and Feldberg<sup>6</sup> to be the common mode



of the "ECE" reaction. The basis given by Amatore and Savéant<sup>5</sup> for assuming the "ECE" mechanism was that  $dE_p/d \log v$ , where  $v$  is the voltage sweep rate during linear sweep voltammetry (LSV), was close to 30 mV according to the theory for a first order process. The concentrations of both substrate and phenol were invariant at  $10^{-3}$  and  $10^{-2}$  M, respectively, in the double potential step chronoamperometric kinetic study.

We have recently added another detail to the reaction of anthracene anion radical with phenol in that  $dE_{zc}/d \log C_{\text{PhOH}}$ , where the subscript refers to the second harmonic *a.c.* zero current crossing potential in this case at a frequency of 10 Hz, was found to be equal to 27.8 mV/decade indicating that the reaction was first order in phenol under the conditions of the experiments.<sup>7</sup> Thus, in the light of the fact that our results supported those of Amatore and Savéant,<sup>5</sup> we considered the mechanism reasonably well established and selected the reaction as a model to use in the development of derivative cyclic voltammetry (DCV) for kinetic studies.<sup>7</sup> We have also found that under some conditions the DCV slope,  $d \ln R'_i/d \ln v^{-1}$ , where  $R'_i$  is the ratio of the derivative peaks on the backward and forward scans of a cyclic voltammogram, was in agreement with that calculated for the ECE<sub>n</sub> mechanism.<sup>8</sup> Thus, it appeared that the mechanism was without complications and it could be used as a model for the ECE<sub>n</sub> reaction.

Recent work from this laboratory has shown that the simple reaction mechanisms proposed for ion radical reactions are generally incorrect and the actual mechanisms are far more complex. A few examples follow. The deprotonation of arylmethyl cation radicals which had been believed to follow the ECE<sub>n</sub> pathway<sup>9,10</sup> has been shown to be far more complex involving several equilibria.<sup>11,12</sup> The proposed carbene anion radical mechanism during the decomposition of diazoalkane anion radical<sup>13-17</sup> has unambiguously been shown to be incorrect.<sup>18-20</sup> The dimer forming reaction during the oxidation of 4,4'-dimethoxystilbene believed to proceed by the cation radical dimerization mechanism<sup>21-22</sup> has been shown to involve predominantly ion radical-substrate coupling.<sup>23</sup> Finally, the electrohydrodimerization of activated olefins

believed to go exclusively by the simple dimerization pathway<sup>24-29</sup> has been found to take place by two different mechanisms neither of which involve anion radical coupling.<sup>30-32</sup> In connection with the latter work, the protonation of methyl cinnamate, a common substrate for electrohydrodimerization studies, in DMF by phenol was found to take place by a very complicated mechanism involving a reversible protonation equilibrium followed by homogeneous electron transfer and further protonation.<sup>33</sup> This suggested that it is necessary to examine the protonation of anthracene anion radical in more detail in order to verify that it is indeed of the simple ECE<sub>n</sub> type or if the complications associated with the methyl cinnamate anion radical protonation are present in this case as well but have gone undetected in previous studies.

In this paper, kinetic studies are described for the reaction of anthracene anion radical with phenol and 2,6-disubstituted phenols using a variety of diagnostic techniques designed to detect any complications in the reaction mechanism.

## RESULTS

### *General features of electrode mechanism analysis.*

A general weakness of electrode kinetic techniques such as cyclic voltammetry, double step chronoamperometry or rotating ring disc electrode voltammetry, to mention three of the most common techniques, is that the reaction orders in substrate and electrode generated intermediate are not easily separable. If the rate law for a process is (6), where the

$$\text{Rate} = k_{\text{obs}} C_B^2 / C_A \quad (6)$$

subscripts refer to the substrate and the intermediate, the reaction kinetics are first order and are easily confused with the more simple rate law (7). This is one of the reasons why incorrect mechanisms are so frequently deduced in this field.

$$\text{Rate} = k_{\text{obs}} C_B \quad (7)$$

On the other hand, LSV slopes are direct consequences of the reaction orders of the various intermediates and substrates.<sup>34</sup> The simple relationships are given by equation (8)–(10) where the reac-

$$dE_p/d \log v = (1/(b+1))RT/nF \quad (8)$$

$$-dE_p/d \log C_A = ((a+b+i-1)/(b+1))RT/nF \quad (9)$$

$$dE^p/d \log C_x = (x/(b+1))RT/nF \quad (10)$$

tion orders are the superscripts in the generalized rate equation (11) and I refers to species formed in

$$\text{Rate} = k_{\text{obs}} C_A^a C_B^b C_I^c C_X^x \quad (11)$$

the process which further participate and X is an additional reactant, such as phenol in the present case. Thus, LSV is the most powerful technique for the analysis of electrode mechanisms and should be applied whenever possible to support results that are obtained by other techniques. One of the reasons that LSV has not been as useful as it is capable of being is that until very recently, it has been a very qualitative procedure. The development of DCV<sup>7</sup> and comparable methods<sup>35</sup> have drastically changed this situation. The practical aspects of quantitative LSV have recently been discussed in detail.<sup>36</sup>

In this paper, LSV is coupled with DCV mechanism analysis<sup>8</sup> in the study of the anthracene anion radical protonation over a wide range of conditions.

*Mechanism analysis with phenol as the proton donor in unbuffered solution.* Data for the voltammetric reduction of anthracene (1.00 mM) in DMF containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) at a mercury electrode at 22 °C in the presence of various concentrations of phenol are summarized in Table 1. The first feature of interest is the way in which  $v_{\frac{1}{2}}$ , which is proportional to the overall rate constant of the reaction and is defined as the voltage sweep rate when the ratio of the peaks on the derivative of a cyclic voltammogram on the backward and forward scans is equal to 0.500,<sup>37</sup> varies with changes in the phenol concentration. The third column gives values of  $v_{\frac{1}{2}}$  normalized to the highest phenol concentration and should be directly proportional to the latter if the reaction order in phenol is unity. This appears

to be the case at the highest concentrations but significant deviation is observed at the lower concentrations. The next feature is that the sweep rate dependence given in the fourth column indicates that the reaction order in anion radical depends on [PhOH] and according to eqn. (8) lies between 1 and 2 in all cases. The value predicted for a reaction order of 1 is 29.3 and 19.5 mV/decade for a reaction order of 2 at 295 K. The final column in Table 1 gives the DCV slope<sup>8</sup> for the case where the switching potential was 300 mV more negative than the reversible potential. The slope calculated for the ECE<sub>n</sub> mechanism under these conditions is -0.351 and that for a reaction with rate law (6) is predicted to be -0.237.<sup>8</sup> The data show that at the highest phenol concentration the analysis is consistent with the simple ECE<sub>n</sub> mechanism but that the mechanism gradually changes with decreasing phenol concentration to one which is nearly purely second order in anion radical at the lowest concentration.

It is obvious that there are complications involved in the mechanism of the protonation of anthracene anion radical by phenol and the two independent techniques agree that the order in anion radical is greater than 1. In addition, the dependence of  $v_{\frac{1}{2}}$  on the phenol concentration suggests that the order in phenol is greater than one in the lower concentration range.

*Kinetic analysis in phenol-phenoxide ion buffers.* An obvious possibility to consider for the anion radical protonation reaction is that the initial step is reversible. This is simply tested by determining the effect of the conjugate base of the proton donor on the kinetics of the reaction. The data in Table 2 show the effect of different phenol-phenoxide buffers on the LSV and DCV slopes as well as on the overall rate as shown in the values of  $v_{\frac{1}{2}}$ . The buffers were prepared by adding Bu<sub>4</sub>NOH in methanol solution to the solutions of anthracene, phenol and

Table 1. LSV and DCV mechanism analyses of the protonation of the anthracene anion radical by phenol in DMF.<sup>a</sup>

| [PhOH]/mM | $v_{\frac{1}{2}}^b/V s^{-1}$ | $v_{\frac{1}{2}}/159 V s^{-1}$ | $dE^p/d \log v^c$ | $d \ln R_1'/d \ln v^{-1d}$ |
|-----------|------------------------------|--------------------------------|-------------------|----------------------------|
| 100       | 159                          | 1.00                           | 24.4              | -0.345                     |
| 40        | 63                           | 0.40                           | 25.4              | -0.315                     |
| 20        | 23.1                         | 0.15                           | 24.7              | -0.289                     |
| 10        | 7.5                          | 0.05                           | 21.0              | -0.236                     |

<sup>a</sup> Substrate (1.00 mM) in solvent containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) at 22 °C at a mercury electrode. <sup>b</sup> The voltage sweep rate at which  $R_1'$  is equal to 0.500 as described in Ref. 37. <sup>c</sup> Obtained from correlations at sweep rates of 100, 200, 400 and 1000 mV s<sup>-1</sup> in mV/decade. <sup>d</sup> The DCV mechanism slope as described in Ref. 8.

Table 2. LSV and DCV mechanism analyses of the protonation of anthracene anion radicals by phenol-phenoxide ion buffers in DMF.<sup>a</sup>

| ([PhOH]/[PhO <sup>-</sup> ])/<br>(mM/mM) | 10/10 |       |       | 20/20 |       |       | 40/40 |       |       | 80/80 |       |       |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|  | 0.50  | 1.00  | 2.00  | 0.50  | 1.00  | 2.00  | 0.50  | 1.00  | 2.00  | 0.50  | 1.00  | 2.00  |
| $dE^p/d \log v^b$                        | 25.0  | 22.7  | 23.5  | 25.5  | 26.1  | 26.1  | 26.0  | 27.6  | 28.0  | 24.4  | 32.0  | 29.1  |
| corr. coef. <sup>b</sup>                 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.999 | 1.000 | 0.998 | 0.999 | 0.999 |
| $v_{\frac{1}{2}}/V s^{-1}$               | 27.0  | 16.0  | 12.3  | 34.3  | 28.8  | 22.3  | 54.9  | 46.6  | 36.8  | 55.4  | 41.6  | 29.9  |
| $-d \ln R'/d \ln v^{-1 d}$               | 0.326 | 0.295 | 0.275 | 0.322 | 0.310 | 0.301 | 0.337 | 0.342 | 0.330 | 0.342 | 0.347 | 0.367 |
| corr. coef. <sup>d</sup>                 | 0.993 | 0.998 | 1.000 | 0.999 | 0.999 | 0.997 | 1.000 | 0.999 | 0.999 | 0.999 | 1.000 | 1.000 |

<sup>a</sup>In solvent containing Bu<sub>4</sub>N<sup>+</sup> (0.1 M) and MeOH (2.34 M) at a mercury electrode at 22 °C. <sup>b</sup>Correlations of data obtained at 100, 200, 400 and 1000 mV s<sup>-1</sup>. Each slope is the result of 20 determinations of E<sup>p</sup>. <sup>c</sup>As defined in Ref. 37. <sup>d</sup>Correlations of the obtained at 10, 20, 50 and 100 V s<sup>-1</sup>, each R' value was the mean of ten replicates.

Bu<sub>4</sub>NBF<sub>4</sub> in DMF. It was therefore necessary to adjust the electrolyte and methanol concentrations so that the ionic strength and [MeOH] did not change. The strategy behind using 1/1 buffer ratios was that if the first step is in equilibrium and only one molecule of phenol is involved before or during the rate determining step, the kinetics would be independent of the buffer concentration. The most obvious test of the latter is the effect of buffer concentration on  $v_{\frac{1}{2}}$ . The overall rate of the reaction increases significantly with increases in the buffer concentration and appears to reach a maximum in the 40/40 buffer. A direct comparison of  $v_{\frac{1}{2}}$  in unbuffered and buffered solution shows that at phenol concentrations of 40, 20 and 10 mM the values were 63, 23.1 and 7.5 Vs<sup>-1</sup> as compared to 46.6, 28.8 and 16.0 when the substrate concentration was 1.00 mM.

Table 3. LSV mechanism analysis of the protonation of anthracene anion radical by 2,6-dimethylphenol in DMF.<sup>a</sup>

| [Anthracene]/mM | [2,6-Dimethylphenol]/mM | (dE <sup>p</sup> /d log v)/mV decade <sup>-1</sup> |
|-----------------|-------------------------|--|
| 0.25            | 10                      | 22.5   |
| 0.50            | 10                      | 19.2   |
| 1.00            | 10                      | 18.3   |
| 2.00            | 10                      | 23.3   |
| 2.00            | 20                      | 24.9   |
| 2.00            | 40                      | 24.9   |
| 2.00            | 80                      | 25.7   |
| 2.00            | 200                     | 26.5   |

<sup>a</sup>In solvent containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) at a mercury electrode at 22 °C. Data were obtained at 100, 200, 400 and 1000 mV s<sup>-1</sup>.

Thus, it appears that the reaction is inhibited by phenoxide ion only in the higher buffer concentration cases. The inhibition becomes increasingly severe at buffers more concentrated than 40/40.

Another interesting feature of the data in Table 2 is that the reaction order in anion radical appears to go to 1 as the buffer concentration is increased. This is indicated by both the LSV and DCV slopes. Another trend in each of the buffers is that  $v_{\frac{1}{2}}$  decreases with increasing substrate concentration.

*The kinetics of the protonation of anthracene anion radical by 2,6-dialkylphenols.* A summary of an LSV analysis of the reduction of anthracene in DMF in the presence of 2,6-dimethylphenol is given in Table 3. The results parallel those observed when phenol was the proton donor. At low phenol concentrations, the reaction order in anion radical is clearly very nearly 2 while it decreases to nearly one as the

Table 4. DCV study of the protonation of anthracene anion radical by 2,6-di-tert-butylphenol in DMF.<sup>a</sup>

| [ROH]/mM           | [Anthracene]/mM | $v_{\frac{1}{2}}/V s^{-1}$ |
|--------------------|-----------------|----------------------------|
| 75                 | 0.25            | 5.70                       |
| 75                 | 0.50            | 6.50                       |
| 75                 | 1.00            | 5.80                       |
| 75                 | 2.00            | 5.40                       |
| 75                 | 4.00            | 5.40                       |
| 150                | 2.00            | 9.80                       |
| 75/75 <sup>b</sup> | 2.00            | 3.70                       |
| 75/75 <sup>b</sup> | 4.00            | 4.60                       |

<sup>a</sup>In solvent containing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) at a mercury electrode at 22 °C. <sup>b</sup>Buffer solution containing equal concentrations of the phenol and the corresponding phenoxide ion.

phenol concentration is increased. These data indicate that the reaction mechanism is qualitatively the same for the two proton donors.

The reaction between the anthracene anion radical and 2,6-di-*tert*-butylphenol is not rapid enough for LSV analysis with  $v$  ranging from 0.1 to 1.0  $\text{V s}^{-1}$ . Therefore, reaction order analysis was carried out by analyzing the effect of concentration changes on  $v_{\frac{1}{2}}$ .<sup>37</sup> The first five rows in Table 4 show that the overall rate constant of the reaction is nearly independent of the substrate concentration. Doubling the proton donor concentration brought about a 1.8-fold increase in  $v_{\frac{1}{2}}$  indicating an approximate first order in the proton donor. The apparent rate constant was significantly decreased in the presence of the corresponding phenoxide ion. The results indicate that the overall reaction is slower with the hindered phenol as the proton donor but here again the mechanism appears to be qualitatively the same as when phenol is the proton donor.

*Apparent activation energies of the protonation reactions.* Since the reaction mechanism for the protonation of anthracene anion radical has been demonstrated to be complex by the data in the preceding sections, it is not possible to evaluate the rate constants. However, it is possible to determine the apparent activation energies without knowing rate constants.<sup>38</sup> The method simply involves eqn. (12) and is a consequence of the fact that  $v_{\frac{1}{2}}$  is directly

$$\ln v_{\frac{1}{2}} = (-E_a/R)(1/T) + c \quad (12)$$

Table 5. Apparent activation energies for the protonation of anthracene anion radicals by phenol and hindered phenols.<sup>a</sup>

| ROH                              | [ROH]/mM | $E_a/\text{kcal mol}^{-1}$ <sup>b</sup> |
|----------------------------------|----------|---|
| Phenol                           | 75       | 9.3                                     |
| Phenol                           | 75       | 8.4                                     |
| Phenol                           | 75       | 8.8                                     |
| Phenol                           | 25       | 8.8                                     |
| Phenol - Phenoxide               | 75/75    | 9.3                                     |
| 2,6-Dimethylphenol               | 75       | 8.2                                     |
| 2,6-Di- <i>tert</i> -butylphenol | 75       | 7.5                                     |

<sup>a</sup> Measured using DCV according to Ref. 38 at a mercury electrode in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M).

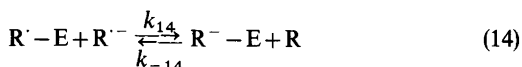
<sup>b</sup> Measurements at a minimum of 3 temperatures in the range, +24 to -17 °C. Correlation coefficients were 0.99 or greater in all cases.

proportional to the apparent rate constant. The value of  $c$  is without significance since it is only a correlation parameter. The data in Table 5 show that the apparent activation energy when phenol is the proton donor is nearly independent of both proton donor concentration and the presence of phenoxide ion with a value of  $8.9 \pm 0.4$  kcal/mol being observed. Values of 8.2 and 7.5 kcal/mol were found when the proton donor was 2,6-dimethyl and 2,2-di-*tert*-butylphenol, respectively.

## DISCUSSION

The study of the mechanisms of the reactions of ion radicals is a fascinating endeavor with no lack of surprises. The protonation of anthracene anion radical by phenol is a very good example of the unexpected results that can be obtained when one begins to probe for the details of the reaction mechanism. All indications before initiating the present investigation pointed to this being a conventional case where the reaction can be described in terms of the simple  $\text{ECE}_h$  scheme.<sup>5,7,8</sup> However, the results described in the preceding section serve to put an end to that elusion. The reaction mechanism is very complex and highly dependent upon the experimental conditions.

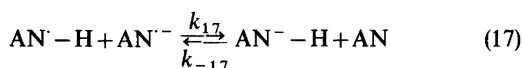
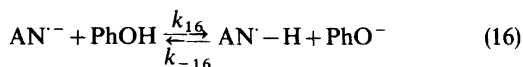
Before going into a deeper discussion of the mechanism of this particular reaction it is worthwhile to attempt to answer a very pertinent question. Why are ion radical reactions so complex? In my opinion, there is a very simple answer to this question. When dealing with these reactions we are always working in a very low concentration range of the reactive intermediates. The reactions generally produce free radicals which are even more reactive than the ion radical itself. To get to final products there must be an oxidation state change and usually a final product forming reaction. The generalized ion radical reaction scheme when radical coupling is not involved is given by eqns. (13)–(15) written for the anionic variety. If the ion radical



concentration is low to start with, the concentration of the neutral radical,  $\text{R}^{\cdot} - \text{E}$ , can be exceedingly

low and even if reaction (14) is diffusion controlled it can be rate determining because of the very low concentrations. The same considerations hold for reaction (15) in which case reaction (14) can be in equilibrium with exceedingly low concentrations of  $R^- - E$  available to take part in (15). The complexity can be even greater if reaction (15) is reversible. The latter is not expected in most cases where the products are uncharged but does occur in some dimerization reactions which produce ionic products.<sup>39</sup>

The product of the electrolytic reduction of anthracene is 9,10-dihydroanthracene.<sup>40</sup> Without making any unreasonable assumptions, we can write the entire reaction scheme leading to the product as in eqns. (16)–(18). No data appear to be available which are of assistance in the estima-



tion of an equilibrium constant for reaction (16). On the other hand, the oxidation of carbanions analogous to  $AN^{\cdot-} - H$  has been observed to take place at potentials more than 0.3 V less negative than that reduce the parent aromatic compounds.<sup>41</sup> This provides an estimate of  $K_{17}$  to be  $>10^5$ . The  $pK_a$  of phenol in dimethylsulfoxide has been estimated<sup>42</sup> to be about 16 and the for  $ANH_2$  would not be expected to differ drastically from that of diphenylmethane (33).<sup>43</sup> It is reasonable to assume that the relative values would be similar in DMF so reaction (18) can be considered to be essentially irreversible.

On the basis of the discussion in the previous paragraph, both  $k_{17}$  and  $k_{18}$  would be expected to approach the diffusion controlled limit for second

order rate constants. Reaction (17) could be slow in spite of this fact if either of  $[AN^{\cdot-} - H]$  or  $[AN^{\cdot-}]$  in the reaction is exceedingly low. This situation is realized when (16) is very far displaced in either direction. Under either circumstance, reaction (17) could be expected to contribute to controlling the overall rate of the reaction. When the total concentration of reactive intermediates, in this case  $AN^{\cdot-} - H$  and  $AN^{\cdot-}$ , is partitioned between the two species which undergo a second order reaction, the rate will be a maximum when equal amounts of the two are present, *i.e.* at any given total concentration.

If reaction (16) were in equilibrium and (18) does not contribute to control of the rate, the observed rate constant of the reaction should be independent of the buffer concentration as long as the buffer ratio is constant. On the other hand, if (16) requires higher  $[PhOH]$  and  $[PhO^-]$  in order achieve equilibrium status, the rate is expected to increase with increasing buffer concentration as long as the latter condition exists.

Most of the trends in the data can be explained in the framework of the foregoing discussion. The increase in apparent rate constant at low buffer concentration could be a consequence that (16) does require higher buffer concentration to come to equilibrium under the reaction conditions. The rate does appear to level off at buffer concentrations of the order of 40 mM. The fact that the reaction is very nearly second order in anion radical at low phenol concentration in unbuffered media may be a consequence of the low concentration of  $[AN^{\cdot-} - H]$ . The apparent reaction order in phenol greater than 1 at low concentrations can be explained if all three reactions (16)–(18) are partially responsible for controlling the rate under those conditions.

The apparent increase in rate in the buffer solutions as compared to the unbuffered solutions at low phenol concentration is not readily explained by the data. However, we must keep in mind that there is a medium change in going to the buffered solu-

Table 6. Rate constants and activation parameters for the protonation of anthracene anion radical by phenols in DMF.<sup>a</sup>

| [ROH]                            | $k/M^{-1} s^{-1}$ | $T/^\circ C$ | $E_a/kcal mol^{-1}$ | $\Delta S^\ddagger/e.u.$ |
|----------------------------------|-------------------|--------------|---------------------|--------------------------|
| Phenol                           | 5,560             | 19.9         | 8.9                 | -13.0                    |
| 2,6-Dimethylphenol               | 2,840             | 19.9         | 8.2                 | -16.7                    |
| 2,6-Di- <i>tert</i> -butylphenol | 288               | 21.7         | 7.5                 | -23.8                    |

<sup>a</sup>Rate constants calculated from  $v_3$  according to Ref. 37.

tions. It was necessary to maintain the concentration of another proton donor, methanol, at a high level (2.34 M) in order to prepare the buffers so that the only variable was the buffer concentration. Thus, this apparent discrepancy could be due to the contribution of methanol to the protonation reaction.

Assuming that reactions (16) and (17) are in equilibrium and the steady state assumption on  $\text{AN}^- - \text{H}$ , leads to rate law (19). Under conditions where the reaction order is 1 in anion radical this must reduce to (20). This being the case, apparent activation energies measured at high phenol con-

$$\text{Rate} = k_{18}K_{16}K_{17}([\text{AN}^{\cdot-}]^2/[\text{AN}])([\text{PhOH}]/[\text{PhO}^-])[\text{PhOH}] \quad (19)$$

$$\text{Rate} = k_{16}[\text{AN}^{\cdot-}][\text{PhOH}] \quad (20)$$

centrations should correspond to  $E_a$  for reaction (16) in the forward direction. Thus, under these conditions the data used in determining the activation energies in Table 5 can be converted using the relationship,  $k=4.31 v_{\ddagger}$ , which is applicable to the  $\text{ECE}_b$  mechanism.<sup>37</sup> The second order rate constants and the activation parameters are summarized in Table 6. The average value of  $E_a$  from Table 5 was used for the phenol reaction. The feature of the most interest in the data is that the  $E_a$  values are not very sensitive to the presence of the hindering groups in the 2,6-positions while the rate constant decreased by a factor of 2 for the methyl substituted phenol and a factor of 20 for the bulky *tert*-butyl substituted proton donor. Thus, it is the entropy of activation,  $\Delta S^\ddagger$ , that is largely responsible for the rate differences. This is not surprising in that the avenue of approach of the anion radical and the hindered phenol leading to a successful collision is greatly restricted as compared to the unsubstituted proton donor. It should also be pointed out that the observed activation energy for a related reaction, the protonation of the methyl cinnamate anion radical by phenol has been observed to equal 9.3 kcal/mol, in close agreement to that observed in this study.<sup>33</sup> This suggests that it is the breaking of the O-H bond that contributes most to the activation energy.

In conclusion, this study has shown that under most circumstances the protonation of the anthracene anion radical by phenol is a very complex process. If the objective of this study were only to find a kinetically simple ion radical reaction, the goal was not achieved. On the other hand, this study

gives a further demonstration that the newly developed analysis methods are capable of unravelling many of the complexities of ion radical reactions.

## EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification were the same as described recently.<sup>7,44</sup> The buffers were prepared by adding the appropriate amounts of a  $\text{Bu}_4\text{NOH}$  solution in methanol (25%), Fluka, to the phenolic DMF solutions.

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