The Reduction of Aromatic Hydrocarbons. I. Polarographic and Electron Spin Resonance Studies of 4,5-Methylenephenanthrene[1]

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Abstract: The effect of proton donors on the polarographic reduction behavior of aromatic hydrocarbons is discussed, and the results of detailed polarographic and electron spin resonance studies of the reduction of 4,5-methylenephenanthrene (RH_2) in DMF and acetonitrile are reported. Polarographic reduction of RH_2 produces the anion radical ($RH_2\cdot^-$) which protonates to some degree to form 9,10-dihydro-4,5-methylenephenanthrene (RH_4) *via* an ece mechanism, even in the absence of any deliberately added proton donor. RH_4 is reduced at a second wave at a more negative potential in DMF but its behavior in acetonitrile is anomalous. Addition of phenol as a proton donor causes the half-wave potentials to shift to more positive values and the limiting diffusion currents to increase in both solvents. The shift of $E_{1/2}$ for the first wave in DMF is in quantitative agreement with the theory of Hoijtink and Peover over its applicable range. It was shown that the presence of even small concentrations of proton donor causes significant shifts in $E_{1/2}$ values. The parent hydrocarbon, RH_2, was itself found to be a proton donor with respect to the anion radical $RH_2\cdot^-$. Coulometric and electron spin resonance studies support the mechanism inferred from the polarographic measurements and, in particular, the conclusion that RH_2 is capable of acting as a proton donor. Esr and visible absorption spectra measurements showed that a complicating side reaction involving molecular oxygen or an oxygen-containing impurity produces 4,5-phenanthrylene ketone on reduction when DMF was used as a solvent. This reaction did not take place in acetonitrile solution.

The importance of the role of possible proton donor species on the electroreduction mechanism of aromatic hydrocarbons has previously been pointed out by several investigators.[2] Significant changes in the polarographic behavior of half-wave potentials, $E_{1/2}$, and limiting currents, i_d, have been observed when concentration changes of electroinert proton donors were made. Also, it has been recently shown that the actual reduction mechanism sequence of aromatic hydrocarbons RH_2[3] involves several interrelated equilibria and reactions following the general scheme

$$\mathrm{RH_2 + e^- \rightleftharpoons RH_2\cdot^-} \qquad (1)$$

$$\begin{array}{lcll}
\text{I}\downarrow & \text{and/or} & \downarrow\text{II} & \\
\mathrm{RH_2\cdot^- + HX \xrightarrow{k_1} RH_3\cdot + X^-} & & \mathrm{RH_2\cdot^- + e^- \rightleftharpoons RH_2^{2-}} & (2) \\
\mathrm{RH_3\cdot + e^- \rightleftharpoons RH_3^-} & & \mathrm{RH_2^{2-} + HX \xrightarrow{k_3} RH_3^- + X^-} & (3) \\
\mathrm{RH_3^- + HX \xrightarrow{k_2} RH_4 + X^-} & & \mathrm{RH_3^- + HX \xrightarrow{k_4} RH_4 + X^-} & (4)
\end{array}$$

and is, thus, considerably more complex than was originally thought.[4]

This paper of this series deals only with sequence I which is a single electron transfer to form an anion radical, $RH_2\cdot^-$, followed by a chemical protonation to form $RH_3\cdot$ which is subsequently reduced itself (in most of these cases the reduction potential of the species $RH_3\cdot$ is more positive than that of the parent, RH_2) and then undergoes another protonation reaction. Thus, an ece-type mechanism is involved. A basic question of the effect on the polarographic characteristics of the rate of protonation (reaction I2) compared to the rate of diffusion of $RH_2\cdot^-$ from the electrode surface is raised when an ece reaction mechanism occurs. Two extremes can be considered. If the proton donor concentration is high and/or the rate constant, k_1, is large, then reaction I2 can be considered to occur at or near the electrode surface, or, if the solution is aprotic or k_1 extremely small, then reaction I2 is a bulk reaction. This paper describes the polarographic behavior which is expected for the above extremes of proton donor concentration and also describes the behavior for intermediate conditions when the rate of the protonation reaction of $RH_2\cdot^-$ is of the same order of magnitude as the rate of diffusion from the electrode surface. An important consideration in this study is the possibility that the hydrocarbon itself as well as the solvent and/or common impurities, such as water, may be proton donors with respect to $RH_2\cdot^-$. It is also possible that the solvent may react with $RH_2\cdot^-$ *via* paths other than I2. All these considerations are important in evaluating the polarographic parameters, such as $E_{1/2}$ and the current constant, $I = i_d/Cm^{2/3}t^{1/6}$,[5,6] and in the significance of correlations of $E_{1/2}$ values with the results of molecular orbital calculations.[7] The aromatic hydrocarbon, 4,5-methylenephenanthrene, RH_2, used in this investigation, has advantages for a detailed study of this kind as its reduction potential varies markedly with proton donor concentration,

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[1] This research was supported in part by grants from the National Science Foundation, NSF GP-6425, and the American Chemical Society, Petroleum Research Fund, PRF 2880-A3,5 and PRF 1941-A5.

[2] (a) G. J. Hoijtink, J. van Schooten, E. DeBoer, and W. I. F. Aalbersberg, *Rec. Trav. Chim. Pays-Bas*, 73, 355 (1954); (b) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960); (c) P. H. Given and M. E. Peover, *Collect. Czech. Chem. Commun.*, 25, 3195 (1960).

[3] The symbol RH_2 is used in this paper for the parent hydrocarbon rather than the usual designation, R, because it is more convenient when discussing reactions where the parent hydrocarbon itself acts as a proton donor.

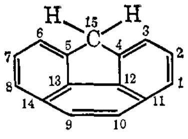
[4] (a) N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, 87, 4529 (1965); (b) *ibid.*, 89, 209 (1967).

[5] All symbols have their usual polarographic meaning.

[6] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954.

[7] A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

and the methylene bridgehead protons are relatively acidic, which makes the hydrocarbon itself a potential proton donor. A disadvantage, however, is that the radical anion, $RH_2\cdot^-$, is capable of side reactions other than proton abstraction in certain solvents, which complicates the interpretation of its polarographic behavior.



RH_2

Electron spin resonance studies wherein radical species which are produced are capable of detection and identification and wherein an estimation can be made of their lifetimes, are a very powerful adjunct in the investigation of a complicated reduction scheme. The results of esr studies of the radical species produced when 4,5-methylenephenanthrene is reduced under a variety of conditions are given in this report.

Previously, Dehl and Fraenkel[8] attempted to generate and detect the radical anion of 4,5-methylenephenanthrene in dimethylformamide (DMF) by electrolytic reduction of a solution of 4,5-methylenephenanthrene at constant potential in a cell positioned above the esr cavity and solution flow through the cavity. They were unsuccessful in obtaining the esr spectrum of $RH_2\cdot^-$ but they did observe the spectrum of the 4,5-phenanthrylene ketyl radical. Dehl and Fraenkel[8] postulated that the ketyl was produced *via* oxidation of the methylene group to the ketone by trace amounts of oxygen in the solution and subsequent reduction of the ketone. In these experiments, oxygen was removed by bubbling dry nitrogen directly from a gas cylinder through the solution.

Janzen and Pacifici[9a] report that the reaction of RH_2 with potassium in tetrahydrofuran (THF) produces the yellow carbanion, RH^-, which can be reduced further to the red dianion radical, $RH\cdot^{2-}$, and Janzen and Gerlock[9b] report that the radical anion, $RH_2\cdot^-$ is formed when sodium is used in THF.

Experimental Section

The dropping mercury electrode (DME) used in these experiments had a drop time of 4.35 sec (open circuit) and 1.80 sec (E_{appl} = −2.50 V *vs.* Ag|AgCl) at a height of 84.0 cm of mercury in a 0.1 *N* *t*-butylammonium perchlorate–DMF solution. Under open circuit conditions, the outflow of mercury was 1.84 mg/sec. An aqueous Ag|AgCl reference electrode was employed throughout all experiments and all potentials are reported with respect to this reference electrode. Electrical contact between reference electrode and the sample solution in the electrolysis cell was made through a salt bridge (asbestos fiber contact) containing the nonaqueous solvent-supporting electrolyte system (which prevents transport of H_2O to the sample cell during the experiment time duration).

The polarograms and coulometry measurements were obtained with a three-electrode electrolysis apparatus based on the operational amplifier circuits of De Ford[10] and were recorded on an Electro Instruments Model 500 X-Y recorder without damping. Spectrophotometry measurements of the electrolysis products were obtained with a Cary 14 spectrophotometer using a specially designed electrolysis flow cell.[11] Solutions were electrolyzed at constant potential at a mercury pool working electrode. The electrolysis solution was allowed to flow past the pool and into a flow quartz spectrophotometer cell. Transport time of the electrolysis products from the mercury pool electrode to the spectrophotometer cell was estimated to be on the order of 1 sec. All solutions were deaerated with nitrogen gas which was purified by passing it through hot copper wool and anhydrous $Mg(ClO_4)_2$ to remove oxygen and water, respectively. The nitrogen gas was also presaturated by bubbling through the solvent. (In the prolonged macroelectrolysis reactions using the flow cell in the coulometric determination of *n* values, the nitrogen was also passed through a MnO–vermiculite column[12] to further reduce trace O_2 impurities. The nitrogen line was all glass except for a short piece of a vacuum rubber tubing which provided the flexible connection between the cell and the outlet of the nitrogen purifying line.)

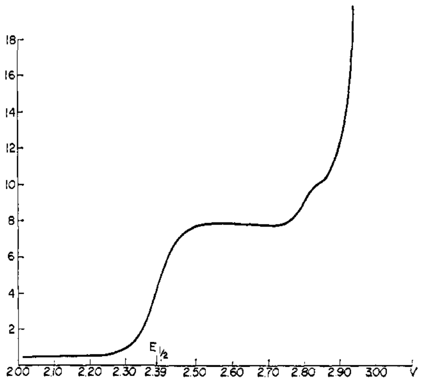


Figure 1. The polarographic behavior of a 2.69×10^{-3} *M* solution of 4,5-methylenephenanthrene in "aprotic" DMF (supporting electrolyte was 0.1 *M* *t*-butylammonium perchlorate).

The 4,5-methylenephenanthrene (RH_2) obtained from the Aldrich Chemical Co. had a melting point of 112–114° and was recrystallized from ethanol. The N,N′-dimethylformamide (reagent grade) was purified by storing over K_2CO_3 for several days, then distilled under reduced N_2 pressure, and kept over Linde Type 4A Molecular Sieves (to further reduce the water content) until required. The acetonitrile (Matheson Coleman and Bell, spectrograde quality) was used without further purification as storage over molecular sieves was found to have no effect on the electrochemistry in this solvent. The *t*-butylammonium perchlorate (*t*-BAP) supporting electrolyte was dried in a desiccator over silica gel for at least 2 weeks. All sample solutions were 0.1 *M* in *t*-BAP. The background currents for both solvents (with *t*-BAP) were small and very smooth as no impurity wave was observed until a decomposition of background was reached with either solvent.

Results and Discussion

Electrochemical Studies. Figure 1 shows that the reduction of RH_2 (in 0.1 *N* *t*-BAP–DMF solution) in the absence of an added proton donor exhibits two waves: a well-defined first wave having a half-wave potential, $E_{1/2}{}^1 = -2.39$ V and a small second wave having an $E_{1/2}{}^2 = -2.78$ V. The addition of phenol[13,14] to the above reaction medium results in

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[8] R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

[9] (a) E. G. Janzen and J. G. Pacifici, *J. Amer. Chem. Soc.*, **87**, 5504 (1965); (b) E. G. Janzen and J. L. Gerlock, *J. Organometal. Chem.*, **8**, 354 (1967).

[10] (a) D. D. De Ford, Analytical Division, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958; (b) W. M. Schwarz and I. Shain, *Anal. Chem.*, **35**, 1770 (1963).

[11] J. Janata and H. B. Mark, Jr., *ibid.*, **39**, 1896 (1967).

[12] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

[13] Phenol has previously been demonstrated to play the role of an electroinert proton donor in the mechanism of the reduction of aromatic hydrocarbons in DMF.[2,3] Santhanam and Bard[14] found that it was difficult to remove trace impurities from phenol which tended to destroy the radical anion. However, in this study we did not find this problem. With phenol present, the decay of $RH_2\cdot^-$ was essentially only by protonation as expected. There was an indistinct wave blended into the background breakdown wave of the phenol-supporting electrolyte solutions. However, it is felt that this wave is the proton discharge wave of phenol and not an impurity.

[14] K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

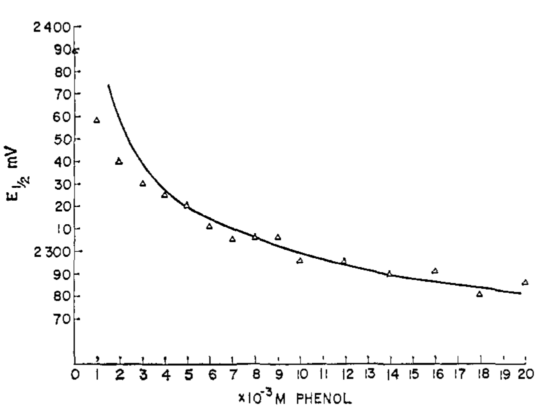


Figure 2. The $E_{1/2}$ *vs.* [phenol] behavior of the first wave of a 1.0 × 10^{-3} *M* 4,5-MP solution in DMF (*t*-BAP = 0.1 *M*). The solid line represents the theoretical response calculated by means of eq 5, and the experimental results are represented by the symbol Δ.

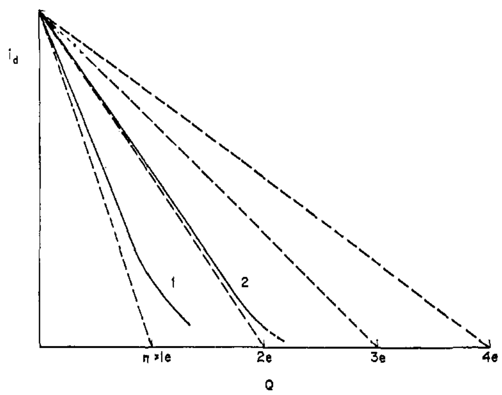


Figure 4. The dependence of the diffusion-limited current of the first wave of a 4,5-MP solution in a 0.1 *M* *t*-BAP–DMF solution as a function of [4,5-MP]: curve 1, [phenol] = 0; curve 2 [phenol] = 8.75 × 10^{-3} *M*.

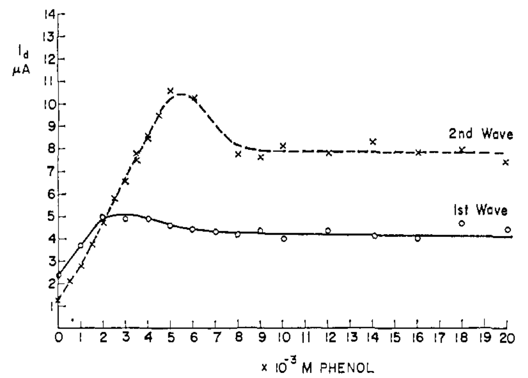
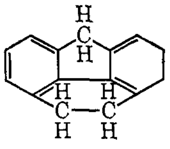


Figure 3. The dependence of the diffusion-limited current of waves 1 and 2 on concentration of phenol (the solvent was DMF and the supporting electrolyte was 0.1 *M* *t*-BAP and [4,5-MP] = 1.0 × 10^{-3} *M*).

positive shifts of the half-wave potentials and an increase in the limiting current of both waves (see Figures 2 and 3). Thus, the nature or mechanism of the polarographic reduction of RH_2 is highly dependent on the concentration of the added proton donor, in this case phenol. At high phenol concentrations the limiting currents of both waves are independent of [phenol] and the ratio of the diffusion currents, i_{d_2}/i_{d_1}, approaches a value of approximately 2.[15]

The limiting current for the second wave, i_{d_2}, increased with increasing concentration of RH_2 itself, both in the absence of phenol and in the presence of a fixed concentration of phenol, as shown in Figure 4. However, the slope of plot of i_{d_2} with [RH_2] was much greater when phenol was present (curve 2) than without phenol (curve 1). In the presence of phenol (Figure 4, curve 2), i_{d_2} is directly proportional to [RH_2] until the concentration becomes large and then the rate of increases tends to level off.

The behavior of the first wave as a function of proton-donor concentration in DMF follows the typical ece behavior of hydrocarbons[1,2] as described in the introduction. The second wave corresponds to the reduction of the compound 9,10-dihydro-4,5-methylenephenanthrene, RH_4 (and not the unlikely possibility of reduction *via* mechanism II), which is itself the product of the ece mechanism given by reaction sequence I. This conclusion was arrived at by a study of the polarographic reduction of 9,10-dihydro-4,5-methylenephenanthrene itself as a function of phenol concentration. The characteristics of the polarographic behavior of this compound were identical with those of the second wave of RH_2.



RH_4

From the fact that an appreciable second wave is observed for RH_2 even when no phenol is present (see Figure 1), it appears that some species already present in the system is capable of acting as a proton donor. This could be the RH_2 itself, the DMF, or some unknown impurity such as water.

Hoijtink, *et al.*,[1] and, later, Given and Peover[2] derived an expression, given below, relating the dependence of $E_{1/2}$ on the concentration of any proton donor [PD], for the reaction path I

$$E_{1/2} = \text{constant} + \frac{RT}{nF} \ln (p - 1) \qquad (5)$$

where p = [PD]/[RH_2]. The term [RH_2] is the bulk concentration of the parent hydrocarbon. Several problematic assumptions were made in the derivation of the above equation: (i) k_2 (rate constant of reaction I4) is greater than k_1 (rate constant of reaction I2), (ii) the diffusion coefficient of the proton donor is the same as that of RH_2, and (iii) the rate of the protonation reaction of $RH_2\cdot^-$ (reaction I2) is very fast compared to the rate of diffusion of $RH_2\cdot^-$ from the electrode surface (the chemical reactions take place at the electrode surface). (Limitations imposed by these will be discussed below.) In addition, eq 5 is defined only for $p > 1$.

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(15) The maxima observed in the i_{d_1} and i_{d_2} *vs.* [phenol] plots of Figure 3 which occur at about 2.5 and 5.5 × 10^{-3} *M* phenol, respectively, are unexplainable at this time. As electrocapillary curves did not indicate any evidence of absorption, it is felt that streaming of the solution at the interface may be occurring in this concentration range which results in abnormally high currents.[14] We feel that the constant current values obtained at high [phenol] and not the maxima represent true diffusion-limited current values for these reductions.

Figure 2 shows a comparison of the experimental dependence of the half-wave potential of the first wave of the reduction of RH_2 as a function of phenol concentration with the calculated values obtained using eq 5 (keeping $[RH_2]$ constant at 1×10^{-3} *M*). The value of the constant in eq 5 was chosen arbitrarily as -2.355 V to normalize the theoretical and experimental lines. It is evident that the agreement of theoretical and experimental values is quite good at high [PD] values ($p > 4$) which indicates that the above assumptions are valid in this region. However, when $p < 4$, the theoretical and experimental points begin to diverge. This probably indicates that at low [PD] values, the rate of diffusion of $RH_2\cdot^-$ from the electrode surface begins to be comparable with the rate of the protonation reaction. However, it is important to note that in the low concentration range of proton donor, the rate of change of $E_{1/2}$ with [PD] is greatest. Thus, even small concentrations of proton donors can cause significant errors in measuring the true $E_{1/2}$ of a hydrocarbon.

The diffusion-limiting currents also changei n this concentration region as shown in Figure 3. At high [PD] values, i_{d_1} is constant but somewhat less than twice the value obtained in the absence of phenol, again indicating along with the small second wave the presence of a finite concentration of some proton donor(s) even in the absence of phenol. Thus, even under "aprotic" conditions[16] in DMF a finite fraction of RH_2 is reduced *via* reaction path I to RH_4 which is then reduced further at wave 2. It is important to note, at this point, curve 1 of Figure 4 (i_{d_2} *vs.* $[RH_2]$ under "aprotic" conditions) also shows a small but finite linear dependence on concentration of $[RH_2]$. This fact, coupled with the facts that the small second wave cannot be reduced in magnitude regardless of how much effort is put into purifying the DMF, the RH_2, the supporting electrolyte, etc., and that the limiting current i_{d_1}, under aprotic conditions is slightly more than one-half that for large proton donor concentrations indicates that some portion of $RH_2\cdot^-$ can be protonated even under "aprotic" conditions. As will be discussed later there is a finite reaction path for the decay of the radical anion

$$RH_2\cdot^- + RH_2 = RH_3\cdot + RH^- \qquad (6)$$

This reaction, however, will not cause any increase in the limiting current as the ratio RH_2:electron remains one.

The fact that the slope of curve 2 of Figure 4 which is a plot of i_{d_2} *vs.* RH_2 begins to decrease at high RH_2 concentration indicates that conditions where the relative rate of diffusion of phenol toward the electrode begins to be the current-limiting factor have been reached.

Similar experiments were carried out using acetonitrile as the solvent. Only one wave was observed with or without added phenol in acetonitrile. The half-wave potential in aprotic acetonitrile was -2.48 V. The current constant, I_{corr}, corrected for the viscosity[17] of the particular solvent was 3.5 for DMF and 3.3 for acetonitrile. This indicates that the first electrode reaction is similar in both solvents. Upon the addition of a sufficient amount of phenol ([phenol] > 7×10^{-3} *M*) the height of the first wave in DMF doubled and the second wave was then two times greater than the first one. Reactions involved in the the first wave (in DMF) stop at RH_4 (two-electron exchange). Entirely different behavior was observed under the same conditions in acetonitrile. The single wave grew with increasing concentration of phenol and reached about 2.5 times the height of its original value. The $E_{1/2}$ potential of this wave shifted to more positive potentials, as expected, but the wave was more drawn out (irreversible appearance).

A likely cause of the difference in behavior of RH_2 in acetonitrile and DMF is the different behavior of 9,10-dihydro-4,5-methylenephenanthrene, RH_4, in these two solvents. No appreciable reduction wave was observed for RH_4 in aprotic acetonitrile but on addition of phenol a poorly defined wave appeared and grew with increasing phenol concentration. The $E_{1/2}$ of this wave at high phenol concentration was -2.39 V which is more positive than the reduction potential of RH_2 itself. In contrast, RH_4 in DMF exhibits a normal reduction wave under aprotic conditions and behaves as expected with varying added phenol concentrations. The $E_{1/2}$ value was -2.65 V in DMF with high concentrations of phenol present, which is quite a bit more negative than the value obtained in acetonitrile.

This indicates that the different behavior of RH_2 in acetonitrile and DMF requires additional study of the different behavior of RH_4 in the two solvents.

The current on constant potential electrolysis in the flow cell was integrated electronically to obtain total charge, *Q*, which was recorded against the i_d of the same electrolysis solution (the diffusion-limited current was obtained using a DME also placed in the flow cell system[11]). The plots should follow the modified Faraday expression

$$i_d = i_{d_0}\left(1 - \frac{Q}{nFVC^0}\right) \qquad (7)$$

where i_{d_0} is the limiting current at $t = 0$, V is the volume of solution, C^0 is the initial concentration of RH_2 in molarity, and n and F have their usual meaning. Several typical experimental i_d *vs.* Q plots are shown in Figure 5. The slope of the experimental i_d *vs.* Q plot is inversely proportional to the number of electrons transferred in the over-all electrode reaction. The dashed lines in Figure 5 indicate calculated i_d *vs.* Q plots to be expected under these experimental conditions for n = 1, 2, 3, and 4, respectively. Experimental curve 1 represents the curve obtained on electrolysis in "aprotic" DMF which indicates that $n = 1$ for the reaction, as was suggested from the polarographic behavior. Under conditions of high phenol concentration, curve 2, $n = 2$ as expected. Thus, the expected products are the $RH_2\cdot^-$ and RH_4 for aprotic, and high [phenol], respectively. The position and shape of the experimental curve 1 indicates, however, that n is actually slightly greater than 1 even during the early portion of the reaction. This is, of course, consistent with the previously proposed idea that there is a finite concentration of

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(16) Aprotic means, hereafter, that the electrolysis solution (solvent, supporting electrolyte, and reactant) are purified with standard practices and *no* proton donor has been added to the system.

(17) $I_{corr} = I\sqrt{\mu}$ where μ is viscosity in millipoise. For DMF—0.1 *M* *t*-BAP, μ = 8.55 mP; for acetonitrile—0.1 *M* *t*-BAP, μ = 3.88 mP. [After T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Amer. Chem. Soc.*, 87, 121 (1965)].

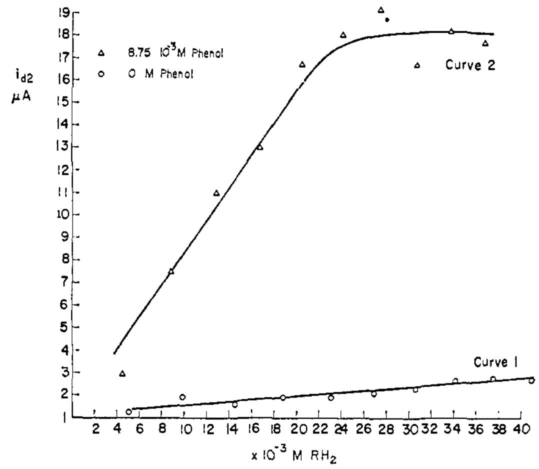

Figure 5. Plot of i_{d_2} for the first wave *vs.* Q for a 1.0×10^{-3} M 4,5-MP solution in 0.1 M *t*-BAP–DMF. The potential of the mercury pool was maintained at −2.50 V: curve 1, [phenol] = 0; curve 2, [phenol] = 2.0×10^{-2} M.

some proton donor present in the DMF even under aprotic conditions.

It was also observed that, after about 70% of conversion, the deviation of curve 1 from $n = 1$ increased. This is partially due to the fact that the background current of the solution becomes an appreciable portion of the total current.

The visible spectrum of aprotic DMF showed a single absorption peak at 395 mμ (yellow solution) which grew during the first 20% of the electrolysis at a potential of −2.5 V. This peak was not, however, observed in aprotic acetonitrile. Beyond 20% of electrolysis in aprotic DMF a new peak at 510 mμ then began to grow as the electrolysis proceeded. (This peak at 510 mμ was also observed in aprotic acetonitrile.) The visible spectrum of this solution was exactly the same as the spectrum of 4,5-methylenephenanthrene anion described in literature.[18] A similar spectrum was obtained by adding the strong base, potassium *t*-butoxide, to a fresh deaerated solution of RH_2. Thus, the red species is undoubtedly RH^-, the anion of RH_2, which has lost a bridge methylene proton.[18] These results substantiate the postulate made previously that the electrolysis product, $RH_2\cdot^-$, is probably reacting also with RH_2 itself which acts as a proton donor (reaction 6). It was found that the peak at 395 mμ in DMF did not change on exposing the solution to air. This observation and the fact that no absorption peak at 395 mμ was found in acetonitrile indicates that the species responsible for absorption at this wavelength is not the radical anion and is peculiar to DMF.

The macroelectrolysis of RH_2 in DMF in the presence of a large excess of phenol yielded an i_d *vs.* Q curve (curve 2 of Figure 5) which indicates that the n value of the reaction is approximately 2 (average value was 2.08) and shows that RH_2 reacts very rapidly at the electrode surface with the proton donor and eventually forms RH_4. Furthermore, the absorption spectrum of this electrolysis solution showed no peak at 510 mμ and only a very small peak at 395 mμ which appears only near the end of the electrolysis reaction. This indicates that the rate of protonation of $RH_2\cdot^-$ by the phenol is very rapid compared to all other decay paths of this anion radical.

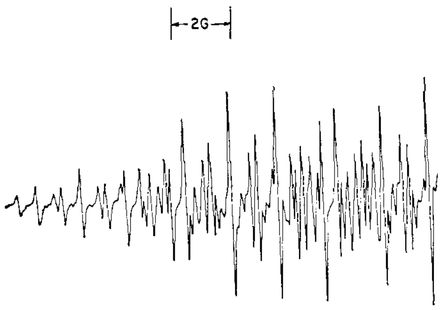

Figure 6. Esr spectrum of 4,5-methylenephenanthrene anion radical, $RH_2\cdot^-$, produced by electrolytic reduction in DMF. The low-field half of the spectrum is displayed.

Electron Spin Resonance Studies. After exhaustive electrolysis in the flow cell used for spectrophotometric and coulometric measurements, which was described above, a portion of the DMF solution was placed in the esr spectrometer, and the spectrum of the 4,5-phenanthrylene ketyl radical was observed.

A 10^{-3} M DMF solution of RH_2 was electrolyzed at a constant potential of −2.0 V *vs.* an aqueous Ag|AgCl reference electrode inside the esr cavity using a modified Varian electrolytic cell assembly. A Varian aqueous solution sample cell was used inside the esr cavity. The esr spectrum observed under these conditions, reproduced in Figure 6, consists of five sets of triplets and is attributed to the 4,5-methylenephenanthrene anion radical. When the electrolysis was carried out at the more negative potential, increasing the electrolysis current, or after a long period of time, the esr spectrum of the 4,5-phenanthrylene ketyl radical was observed.

An experiment similar to the one performed by Dehl and Fraenkel,[8] and using a similar electrolysis cell, in which a 10^{-3} M solution of RH_2 in DMF was electrolyzed at constant potential with the electrolysis cell situated above the esr cavity and solution allowed to flow through the cavity at a maximum rate of about 5 ml/min, reproduced the results of Dehl and Fraenkel[8]—only the esr spectrum of the ketyl radical was observed. The ketyl radical is very stable. When electrolysis and flow of solution were stopped, the lifetime of the ketyl radical was many hours.

When a 10^{-3} M acetonitrile solution of RH_2 was electrolyzed (at a potential of −2.4 V) in the cell above the esr cavity using exactly the same procedure as for the DMF solution, an esr spectrum identical with that which was obtained when a DMF solution was reduced *in situ* and which was attributed to $RH_2\cdot^-$ was observed. Under these conditions the radical $RH_2\cdot^-$ is fairly unstable. The esr spectrum of this species could only be obtained when close to the maximum solution flow rate was used. When $RH_2\cdot^-$ decayed, however, no other radical species was detected. The decay of $RH_2\cdot^-$ in acetonitrile did not produce the stable ketyl radical.

We also caused 4,5-methylenephenanthrene to react with sodium and potassium in THF, and our results agree with those already reported by Janzen and

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(18) (a) A. Streitwieser, Jr., and J. I. Brauman, *J. Amer. Chem. Soc.*, **85**, 2633 (1963); (b) A. Streitwieser, Jr., J. I. Brauman, J. H. Hamonns, and A. H. Pudjaatmaka, *ibid.*, 87, 384 (1965); (c) E. C. S. Steiner and J. M. Gilbert, *ibid.*, 87, 382 (1965).

Gerlock.[9b] On reduction with K we get the dianion radical $RH\cdot^{2-}$, while with Na a radical is formed whose esr spectrum is essentially identical with the spectrum of $RH_2\cdot^-$ observed in the case of *in situ* electrolytic reduction of a DMF solution. When a small amount of $RH_2\cdot^-$ was formed by Na reduction in THF in the presence of a large excess of RH_2, the radical decayed rapidly. A similar observation was reported by Janzen and Gerlock.[9b] A 10^{-2} *M* solution of RH_2 in THF was completely reduced with sodium, and evidence for the formation of gaseous hydrogen was sought by placing the sample inside a microwave discharge coil. No hydrogen emission lines were observed.

We shall first show that a comparison of the proton hyperfine splitting of the radical species, observed in this work (see Figure 6), with the splittings of similar radicals previously reported leads to an unequivocal identification of the species as the 4,5-methylenephenanthrene anion radical.

The proton splitting constants of phenanthrene anion radical, the proposed 4,5-methylenephenanthrene anion radical, and the dianion radical of 4,5-methylenephenanthrene are all quite similar, while those of the 4,5-phenanthrylene ketyl radical are quite different. The values of these proton splittings are given in Table I.

Table I. Hyperfine Splitting Constants in Gauss

	Position[a]					
Radical	9,10	1,8	3,6	2,7	4,5	15
$RH_2\cdot^-$ [b]	5.27	3.55	3.06	0.63		1.51[c]
$RH\cdot^{2-}$ [d]	5.13	3.15	3.15	0.57_5		0.37_5[e]
$RH\cdot^{2-}$ [f]	4.96	3.02	3.02	0.53		0.36[e]
Phenanthrene radical ion[g]	4.43	3.71	2.88	0.63	0.43	
4,5-Phenanthrylene ketyl ion radical[h]	0.10	3.06	2.12	0.03		

[a] See figure in text for numbering system. Assignment of splittings based on previously reported work and molecular orbital calculations. [b] $RH_2\cdot^-$ = 4,5-methylenephenanthrene anion radical. Electrolytic reduction in DMF. This work. [c] Methylene splitting. Assigned on basis of deuteration. [d] $RH\cdot^{2-}$ = 4,5-methylenephenanthrene dianion radical. Potassium reduction in THF. This work. [e] Doublet splitting. [f] Potassium reduction in THF: E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, **70**, 021 (1966). [g] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963). [h] Electrolytic reduction in DMF; see ref 8.

This behavior is to be expected. All four of these radicals have a plane of symmetry through the center of the molecule and therefore for each radical a number of the molecular orbitals used for the π electrons will be antisymmetric with respect to this plane. For these orbitals the symmetry plane is then a nodal plane for the electron density. If one uses, for example, a simple Hückel molecular orbital treatment, then all the antisymmetric orbitals of phenanthrene will remain unchanged on addition of a group on the symmetry plane. In an aromatic hydrocarbon anion radical, the unpaired electron occupies the lowest antibonding orbital of the parent hydrocarbon, and for phenanthrene this is an antisymmetric orbital. We would expect that addition of a group on the symmetry plane of phenanthrene, unless that group were highly electron attracting, would result in a lowest antibonding orbital which was precisely the same antisymmetric lowest antibonding orbital as in phenanthrene. Thus, one would expect for both the anion and dianion radicals of 4,5-methylenephenanthrene that the unpaired electron would occupy the same molecular orbital as in phenanthrene anion radical to a first approximation. In the ketyl radical, however, we have a strongly electron-attracting group substituted on the symmetry plane of phenanthrene, and we might expect that the order of orbital energies in this case to be altered so that the lowest antibonding orbital is symmetric. This would allow the unpaired electron to occupy an orbital with high electron density on the symmetry plane which contains the electron-attracting group.

Hückel molecular orbital calculation, using Coulson and Crawford's[19] parameters for the methylene group and the parameters used by Dehl and Fraenkel[8] for the ketyl group, yields results in complete agreement with our expectations—the unpaired electron in the anion and dianion radicals of 4,5-methylenephenanthrene is placed in the same antisymmetric orbital as for the phenanthrene anion radical, while in the ketyl radical the lowest antibonding orbital is a symmetric orbital with quite a different electron distribution.

Thus, the observation that a radical species is formed in DMF on constant potential electrolytic reduction *in situ* at −2.3 V, which is below the half-wave potential, −2.4 V, for the first polarographic wave of 4,5-methylenephenanthrene in DMF, and the fact that the esr spectrum of this radical exhibits five sets of triplets with hyperfine splittings completely consistent with our expectations for 4,5-methylenephenanthrene anion radical, leaves little doubt that the first polarographic wave for the reduction of 4,5-methylenephenanthrene in DMF corresponds to the one-electron reduction to form the anion radical.

The observations that (i) the esr spectrum of $RH_2\cdot^-$ could be observed when RH_2 in acetonitrile was reduced in an electrolysis cell situated above the esr cavity but that the ketyl was formed when DMF was used as a solvent under identical conditions and (ii) no ketyl was observed on the decay of $RH_2\cdot^-$ in acetonitrile indicates that the source of oxygen is peculiar to the DMF solution.[20] This different behavior in DMF and acetonitrile indicates that the standard purification and deaerating procedures used for DMF solutions leave the solution still capable of complicating side reactions involving oxygen which are not possible in acetonitrile.

The ability to detect the esr spectrum of $RH_2\cdot^-$ in DMF if one uses reduction *in situ* while on reduction in the electrolysis cell situated above the esr cavity only the spectrum of the ketyl is observed is understandable if one recognizes that a molecule reduced at the electrode surface can suffer quite a different fate before it is inside the sensitive region of the esr cavity in the two cases.

As previously mentioned by Janzen and Gerlock,[9b] the fact that the stability of $RH_2\cdot^-$ in THF decreases in the presence of large amounts of the parent RH_2 supports the contention that the hydrocarbon RH_2 itself may be a potent proton donor with respect to the anion radical. Some further evidence supporting this argument may come from the observation that the line

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(19) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(20) We note that the yellow species with absorption at 395 mμ observed in DMF is not due to 4,5-phenanthrenyl ketone, since the latter species was observed to have a single absorption peak at 370 mμ.

widths in the esr spectrum of $RH_2\cdot^-$ produced electrolytically are quite narrow even under conditions of incomplete reduction so that moderate amounts of unreduced RH_2 are also present.

One expects broad lines in the esr spectrum of a hydrocarbon anion radical when the parent hydrocarbon is also present due to reversible electron transfer between these species. If there is no special reason for the rate of this electron-transfer reaction to be especially slow in the case of 4,5-methylenephenanthrene, then the narrow lines which are observed for the anion radical in the presence of the parent hydrocarbon may be attributed to irreversible radical decay caused by proton transfer from the hydrocarbon to the radical competing with the reversible electron-transfer process which causes line broadening.

Conclusions

It is evident from the results discussed above that conditions normally considered to be aprotic are not in reality so with respect to the reduction of 4,5-methylenephenanthrene. When an ece-type mechanism involves a chemical product of a proton exchange with a higher electron affinity than the parent species, the proton-donor nature of the solvent, parent hydrocarbon itself, and possible hard-to-remove impurities are very important in studying the electrochemical parameters, half-wave potential, and diffusion-limiting current. The study of the 4,5-methylenephenanthrene system showed that even under careful purification of solvents to give aprotic conditions, evidence for a persistent ece mechanism is found. The reaction of the anion radical, $RH_2\cdot^-$, in both DMF and acetonitrile was found to be rapid enough to produce, even under aprotic conditions, an appreciable ece component to the over-all reaction mechanism. This fact is especially important when one is measuring a half-wave potential for the purpose of making correlations with the results of molecular orbital calculations. One of the objects of this study was to point out that if an ece mechanism occurs, the measured half-wave potential may be seriously different from that for the couple $RH_2 + e^- \rightleftarrows RH_2\cdot^-$ needed for theoretical correlations (eq 5 and Figure 2 show that $E_{1/2}$ varies most significantly when the proton-donor concentration is small).

The problem is complicated even further when side reactions with $RH_2\cdot^-$ to form a different parallel ece reaction path other than sequence I occur, even in presumably inert solvent systems, such as DMF. The possibility of side reactions further serves to emphasize the fact that it is absolutely necessary to understand completely the total electrode process before using a polarographic parameter in a theoretical correlation.

Although the nature of the electrode processes taking place during the reduction of 4,5-methylenephenanthrene in DMF (under both aprotic and high proton-donor concentrations) and the one wave in acetonitrile under aprotic conditions was elucidated by this study, the reaction of RH_2 in acetonitrile in the presence of high concentrations of phenol is not understood.

The Chemistry of Ylides. XVIII. A ^{19}F Nuclear Magnetic Resonance Study of Electronic Interactions in Phosphonium Salts, Ylides, and Oxides

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Abstract: Examination of the ^{19}F nmr spectra of the oxide, methyl salt, and ylide derivatives of tris(fluorophenyl)-phosphine has permitted an assessment of the inductive and conjugative electronic interactions by and with tetravalent phosphorus. Inductive interactions seem dominant in these systems. Conjugative ($p\pi$–$d\pi$) interactions of tetravalent phosphorus with an adjacent anionic center appear to rule out substantial conjugative interaction between the phosphorus and an attached aryl ring.

Although phosphonium ylides have been known for over 50 years and have been widely used in synthetic organic chemistry (*i.e.*, the Wittig reaction) for 15 years, only within the last 4 years have such ylides been subjected to physical studies in an effort to learn more of their molecular structure and electronic properties.[2] Our interest in the latter aspect was excited by the observation[3] that triphenylphosphonium ylides ($Ph_3P{=}CR_2'$) were less basic and less nucleophilic than the corresponding trialkylphosphonium ylides ($R_3P{=}CR_2'$). It seemed to follow that there was more $p\pi$–$d\pi$ overlap between the carbanion and phosphorus in the former ylides, indicating that the phenyl groups on phosphorus were electron-withdrawing relative to the alkyl groups.

As a follow up to that observation, recently we have explored the effect of aryl substituents on the basicity of fluorenylidenetriarylphosphoranes (I, R = C_6H_4–X).

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[1] (a) Author to whom inquiries should be addressed at the University of North Dakota, Grand Forks, N. D. 58201. (b) The nomenclature used in this paper is contrary to that defined by the author in ref 2. The change was made to conform to current indexing practices of *Chemical Abstracts* and to ensure a consistent usage in journal practice.

[2] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 7–189.

[3] A. W. Johnson and R. B. LaCount, *Tetrahedron*, 9, 130 (1960).