Kinetics of Rapid Reactions Coupled to Charge Transfer at Electrodes. Reactions of Anthracene Cation Radicals with Pyridine

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The mechanism of the reaction between 9,10-diphenylanthracene cation radical and pyridine was examined by linear sweep voltammetry. The reaction was found to be second order in the cation radical and first order in pyridine confirming a recent homogeneous kinetic study. On the other hand, the independence of the peak potential on the substrate concentration indicates a complex mechanism with a rate law having the substrate concentration in the denominator. The latter rules out rate determining electron transfer which was recently proposed for the reaction mechanism. The voltammetric data is most consistent with the complexation mechanism (i) to (iii). Reactions of 9-phenylanthracene and anthracene cation radicals

$$DPA^{\cdot+} + P \rightleftarrows DPA^{\cdot+}/P \qquad (i)$$

$$DPA^{\cdot+}/P + DPA^{\cdot+} \rightleftarrows DPA^{2+}/P + DPA \qquad (ii)$$

$$DPA^{2+}/P \rightarrow DPA^{\pm}P^{+} \qquad (iii)$$

with pyridine probably involve similar mechanisms but sufficient evidence is lacking for definite assignment.

A number of well-established kinetic techniques, including double-step chronoamperometry,[1] chronabsorptometry[2] and rotating ring disc electrode voltammetry[3] exist for the determination of the rate constants of homogeneous chemical reactions following charge transfer at electrodes. These methods involve the generation of the reactive intermediates at potentials sufficiently great that

charge transfer is diffusion controlled. The effect of the chemical reaction upon the current or the absorbance due to the reactive intermediate is monitored and rate constants are then obtained by fitting experimental data to theoretical working curves. The upper limit for rate constants determined by these methods is of the order of 10^4 s^{-1}. The first two methods are limited by the time necessary to charge the electrical double layer at the electrode-solution interface while the latter method is limited by practical considerations in design and rotation rates.

Many of the reactions of ion radicals and most of those of doubly charged ions of organic compounds are too rapid to be studied by the methods mentioned above. In principle, the kinetic shift in peak potentials during linear sweep voltammetry (LSV)[4,5] should yield rate constants for very rapid reactions providing that charge transfer kinetics do not interfere. Recently, the use of theoretical relationships without experimental calibration was challenged when it was found that kinetic potential shifts during LVS measurements on the oxidation of 9,10-diphenylanthracene (DPA) in the presence of pyridine (P) were much smaller than predicted for the eCe type of mechanism.[6] The basis for this challenge was that the mechanism was considered to be established since homogeneous kinetic studies[7,8] had indicated that the reaction was first order in both DPA$^{\pm}$ and pyridine, a situation for which theory predicts a 29.6 mV change in potential for a decade change in pyridine concentration rather than the 17 mV change that was observed.[6] However, the situation must now be reexamined

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since Evans and Blount[9] have reported that the reaction is second order in DPA$^{\cdot+}$ when the latter is present in low concentration, as it is during slow LSV. In this paper we present the results of a reinvestigation of the reaction between DPA$^{\cdot+}$ and pyridine by LSV along with data for reactions of pyridine with the cation radicals of anthracene (AN) and 9-phenylanthracene (PA).

RESULTS

Measurement techniques. In the previous work[6] the advantages of second harmonic AC voltammetry for the measurement of the kinetic potential shift during LSV was pointed out. The principle advantages are the precision with which zero current crossing potentials can be measured and the

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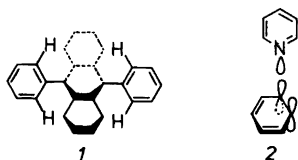
near independence of the response on the solution uncompensated resistance.[9] More recently, we have described precise peak potential measurements during LSV by analog differentiation of the current-voltage curves[10] as previously reported by Perone.[11] The precision of the two methods appears to be comparable and both are very significant improvements over ordinary peak potential measurements. Both methods have been used extensively in this work. In order to assign values to rate constants by the LSV method, the value of the reversible potential must be known, and for this purpose phase selective second harmonic AC voltammetry is the measurement method of choice. The use of this technique on rapidly reacting redox systems has recently been discussed in detail.[12]

Kinetic methods. For purely kinetic waves, *i.e.* when the charge transfer is fast relative to the rate of the chemical follow-up reactions and to the voltage sweep rate v, the electrode peak potential (E^p) during LSV is affected by a number of experimental variables to a degree dependent upon the mechanism of the electrode reaction.[4,5,13-17] The theoretical dependence of E^p on the variables can be expressed as integral fractions of RT/nF as follows:

$$\delta E^p/\delta \log v = (\ln 10)(RT/nF)/a \qquad (3)$$

$$\delta E^p/\delta \log C^o = (\ln 10)(RT/nF)/b \qquad (4)$$

$$\delta E^p/\delta \log C^x = (\ln 10)(RT/nF)/c \qquad (5)$$

In the equations C^o refers to the substrate concentration, C^x to the concentration of an additional reactant, R is the gas constant, T the temperature in K and F is the faraday constant. The integers, a, b and c, are dependent upon the electrode mechanism.

Mechanism analysis by LSV thus consists of determining the values of a, b and c and comparing them with those predicted by theoretical analysis of the mechanisms.[4,5,13-17] Rules for predicting the values of a, b and c without calculation have recently been suggested.[18]

The dependence of pyridine concentration. Second harmonic AC voltammograms recorded during the oxidation of DPA in acetonitrile containing pyridine (4.2 mM) are illustrated in Fig. 1. Under the conditions of the experiment, a frequency of 500 Hz was sufficient to "outrun" the reaction so that the I (in phase) and Q (quadrature) components of the second harmonic AC current intersected at zero current, defining the reversible potential (E^{rev}). The voltammograms recorded at 8 Hz no longer intersected at zero current and the potential where the Q component crossed zero current was shifted 22 mV from E^{rev}. Increasing the pyridine concentra-
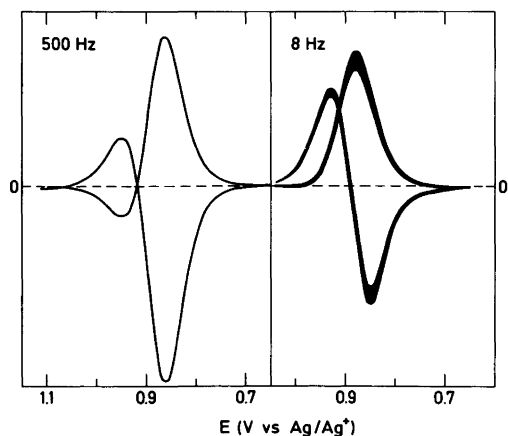
Fig. 1. Phase selective second harmonic AC voltammograms for the oxidation of DPA in acetonitrile containing pyridine (0.0042 M). Voltage sweep rate = 10 mV s^{-1}.

Table 1. Kinetic potential shifts for the oxidation of 9,10-diphenylanthracene in acetonitrile containing pyridine at 20 °C.[a]

Run	0.00827[b]	0.0207[b]	0.0413[b]	0.0827[b]	Slope[c]	Correlation coefficient
1	11.89	20.61	25.49	31.05	19.1	0.998
2	12.90	20.34	25.70	31.66	18.7	0.999
3	12.68	20.08	25.52	31.32	18.6	1.000
4	13.58	19.70	26.26	30.74	17.7	0.997
5	13.57	20.49	25.85	32.29	18.7	0.999
Average	12.92($\pm$0.70)	20.24($\pm$0.36)	25.76($\pm$0.31)	31.41($\pm$0.60)	18.6($\pm$0.5)	

[a] Kinetic potential shifts, ΔE, are the differences between E^{rev} and the second harmonic AC quadrature zero current crossing potentials expressed in mV and measured at 10 Hz and 10 mV s^{-1}. [b] Pyridine concentration. [c] Least squares treatment of the data, $x = \log$ (pyr) and $y = \Delta E$.

Table 2. Kinetic potential shifts for the oxidation of 9-phenylanthracene in acetonitrile containing pyridine at 20 °C.[a]

Run	0.00413[b]	0.00827[b]	0.0207[b]	0.0413[b]	Slope[c]	Correlation coefficient
1	100.23	107.55	112.99	119.31	18.6	0.994
2	100.11	107.63	114.39	118.55	18.6	0.993
3	102.07	108.99	116.15	119.91	18.0	0.994
4	100.01	108.09	113.69	119.37	18.9	0.992
5	100.25	108.01	115.13	119.45	19.3	0.993
Average	100.53($\pm$0.86)	108.05($\pm$0.57)	114.47($\pm$1.23)	119.32($\pm$0.49)	18.7($\pm$0.5)	

[a] Kinetic potential shifts, ΔE, are the differences between E^{rev} and the second harmonic AC quadrature zero current crossing potentials expressed in mV and measured at 10 Hz and 10 mV s^{-1}. [b] Pyridine concentration. [c] Least squares treatment of the data, $x = \log$ (pyr) and $y = \Delta E$.

tion resulted in a further shift of the Q component zero crossing potential and the magnitude of the shift was observed to be linearly related to the pyridine concentration as expected from (5).

Data for five sets of experiments where the pyridine concentration was varied from 0.00827 to 0.0827 M during the oxidation of DPA in acetonitrile are summarized in Table 1. The AC frequency was 10 Hz and the DC voltage sweep rate was 10 mV s^{-1}. The tabulated values are the differences between E^{rev} and the second harmonic AC Q component crossing potentials (E^Q) and are the average of five measurements. A comparable set of five experiments on the oxidation of PA in acetonitrile containing pyridine was carried out and the data can be found in Table 2. The values in parentheses represent one standard deviation of replicate determinations from the average values. Least squares analyses of the data sets were carried

out and the correlation coefficients are tabulated. The average values of the slopes were found to be 18.6$\pm$0.52 for the reaction of DPA$^{\cdot+}$ and 18.7$\pm$0.44 for that of PA$^{\cdot+}$, indicating that the value of c in (5) is 3, which predicts a slope of 19.4 mV at 20 °C.

Several sets of experiments were conducted on the oxidation of AN in acetonitrile containing pyridine. The range of nucleophile concentrations used, 0.00827 to 0.0413 M, was limited by severe filming on the electrode at higher concentrations. Slopes ranging from 21.7 to 14.7 with an average of 17.2 mV were observed. The poor reproducibility can readily be explained by the uncertainty in the measurements. The reason for the greater uncertainty in the measurement of the potentials in this case is connected with the electrode filming problems. The fact that the concentration range was very limited contributes to a larger uncertainty in the slope as well. The average value is still close to

Table 3. Voltage sweep rate dependence for kinetic potential shifts during oxidation of 9,10-diphenyl-anthracene in acetonitrile containing pyridine at 20 °C.[a]

[DPA][b]/mM	Slope/mV[c] per decade	Correlation coef. [d]
0.05	19[e]	
0.10	19[e]	
0.10	20.8[f]	0.9943
0.20	27.0[f]	0.9998
0.40	28.6[f]	0.9998
1.00	28.5[f]	0.9970

[a] Pyridine concentration equal to 12.4 mM. [b] Substrate concentration. [c] Slope obtained for plots of E^p vs. log v. [d] From linear regressions analysis. [e] Measured at only two sweep rates, 100 and 1000 mV s^{-1}. [f] Measurements at 100, 200, 400 and 1000 mV s^{-1}. Each potential used in the correlation was the average value of 15 determinations.

that observed for DPA and PA and thus it seems safe to conclude that c is equal to 3 in this case also.

Sweep rate and substrate concentration dependence. At a pyridine concentration of 12.4 mM and an applied AC frequency of 30 Hz, the difference in zero current crossing potentials at 10 and 100 mV s^{-1} was found to be equal to 19.3 mV at 22 °C during the oxidation of DPA in acetonitrile indicating that a in eqn. (3) is equal to 3 for that reaction. A more extensive investigation of the effect of v was carried out using the differentiated DC response and these results are summarized in Table 3. Voltage sweep rates of 100, 200, 400 and 1000 mV s^{-1} were used over a concentration range of 5×10^{-5} to 10^{-3} M. Slopes ranging from 28.5 down to 19 mV were observed indicating that a varies from 2 to 3 over the concentration range investigated. The data for the lowest concentration in Table 3, 0.05 mM, was taken only at two sweep rates, 100 and 1000 mV s^{-1} and it was necessary to measure peak potentials on the derivative voltammograms rather than the zero crossing points due to interfering background processes. Under comparable conditions, the sweep rate dependence for both PA and AN appears to be close to 29 mV/decade.

The potentials measured at 1000 mV s^{-1} for all of the concentrations of DPA listed in Table 3 did not vary more than 1.0 mV which indicates that b in eqn. (4) is equal to 0. Potentials measured for PA

and AN under similar conditions were also found to be independent of the substrate concentration.

DISCUSSION

The reaction between DPA$^+$ and pyridine is one of the most thoroughly investigated processes following charge transfer at an electrode. The initial rotating disc electrode study led to the conclusion that the mechanism could be represented by equations (6) to (9) with reaction (7) rate determining.[19] Spectroelectrochemical studies supported this mechanism assignment[20] and the homogeneous kinetic studies[7,8] confirmed that the reaction is first order in both DPA$^{.+}$ and pyridine. Thus, the evidence for this mechanism appeared to be unquestionable. It was with this background that the reaction was suggested as a means of calibrating the LSV method to improve the reliability of the rate constants obtained.[6] The recent observation of kinetics second order in DPA$^{.+}$ when the reaction

$$(6)$$
$$(7)$$
$$(8)$$
$$(9)$$
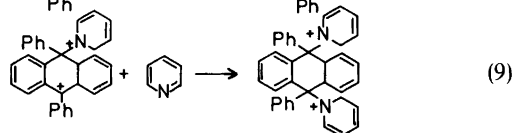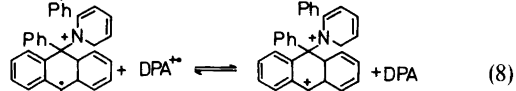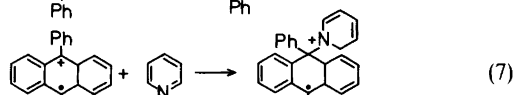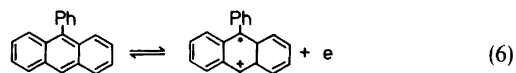
was studied at low radical ion concentration[9] sheds doubt on all of the previous mechanistic studies and removes the reaction from the small list of those for which the mechanism is firmly established. It is somewhat ironic that Marcoux[21] had earlier, on the basis of chronoamperometric experiments, suggested a second order mechanism which was ruled out by the homogeneous kinetic studies.[7,8]

The mechanism proposed by Evans and Blount[9] includes the steps illustrated by eqns. (6) to (9) with (7) as an equilibrium and (8) the rate determining step. The LSV response for this mechanism has been treated theoretically and the values of a, b,

and c (eqns. 3—5) are predicted to be equal to 3 and the three slopes to be 19.7 mV/decade at 25 °C.[13] Thus, the observation that b in eqn. (4) is equal to 0 over the entire concentration range studied effectively rules out this most recently[9] suggested mechanism.

An alternative mechanism for cation radical reactions has been postulated in a number of related cases.[22–24] The essential difference in this mechanism and that shown in eqns. (6)—(9) is that the initial reaction between the cation radical and the nucleophile (10) is viewed as the formation of a π complex which can react unimolecularly to form

$$DPA^{\cdot +} + P \rightleftarrows DPA^{\cdot +}/P \tag{10}$$

$$DPA^{\cdot +}/P \rightarrow DPA^{\cdot} - P^{+} \tag{11}$$

$$DPA^{\cdot +}/P + DPA^{\cdot +} \rightleftarrows DPA^{2+}/P + DPA \tag{12}$$

$$DPA^{2+}/P \rightarrow DPA^{\pm}P^{+} \tag{13}$$

the sigma complex (11) or undergo oxidation (12) to give the dication complex which then reacts further to give product (13). Steady state analysis of this mechanism under conditions where (11) is not important, i.e. when the reaction is second order in cation radical, and assuming that (10) and (12) are rapid equilibria results in rate law (14) where

$$-d[DPA^{\cdot +}]/dt = k_{app}[DPA^{\cdot +}]^{2}[P]/[DPA] \tag{14}$$

k_{app} is equal to $2K_{10}K_{12}k_{13}$. This rate law is in fact the same as for the disproportionation mechanism, for which the LSV response has been analyzed.[14] The values of the LSV slopes for this mechanism are predicted to be 19.7, 0, and 19.7 mV/decade (eqns. 3, 4, and 5, respectively) which is precisely what is observed for the oxidation of DPA in the presence of pyridine, providing that [DPA] is low.

It should be pointed out that since (14) is also the rate law for the disproportionation mechanism previously proposed by Marcoux[21] that the LSV response is equally consistent with that mechanism. However, arguments have already been set forth based on the energetics of the reaction which makes that mechanism doubtful.[25] Furthermore, the contribution of the disproportionation mechanism would be expected to be greatest at high [$DPA^{\cdot +}$] and it is under these conditions that kinetics first order in the cation radical are observed.

Since the sweep rate dependence for PA and AN in the presence of P was not that predicted by a second order mechanism under any of the conditions studied, we hesitate at this time to propose a mechanism for these reactions. It should also be pointed out that an inconsistency still exists for the $DPA^{\cdot +}$/P reaction and that is that Evans and Blount[9] did not find the [DPA] dependence predicted by eqn. (14). Thus, the LSV data rule out rate determining electron transfer but the homogeneous kinetic study does not confirm the alternative π complex mechanism. At this point we can only suggest that reactions (10)—(13) best describe the voltammetric results and that further detailed studies with other substrates such as PA and AN are necessary before attempting to assign rate constants to the reactions.

EXPERIMENTAL

Reagents, electrodes and cells. Reagent grade anthracene, 9,10-diphenylanthracene and 9-phenylanthracene were recrystallized before use. Reagent grade pyridine was used as obtained. Acetonitrile was passed through a column of neutral alumina, refluxed over phosphorus pentaoxide for several hours and distilled slowly. The water content was estimated to be less than 1.0 mM before adding the supporting electrolyte. Tetrabutylammonium tetrafluoroborate was prepared by ion exchange from the hydrogen sulfate (Hässle, Gothenburg), precipitated from dichloromethane with diethyl ether and dried. The working electrodes were prepared by sealing small diameter platinum wire in glass and polishing to a planar surface as previously described.[26] Reference electrodes were $Ag/AgNO_3$ (0.01 M) in acetonitrile constructed in the manner described by Moe.[27] Leakage from the reference electrodes was negligible as was the current flow using the small electrodes which enabled us to use a single compartment cell consisting of a cylindrical tube (25 ml volume) fitted with a joint to accomodate a teflon electrode holder equipped with a tube for the inlet of purified nitrogen.

Instrumentation. The potentiostat was a PAR model 173D driven by a PAR 175 function generator. Either a PAR 5203 lock-in amplifier with built-in oscillator or a PAR 129A lock-in amplifier together with a PAR 189 selective amplifier/oscillator were used as phase sensitive detectors. Analog differentiation was accomplished using the PAR 189 selective amplifier. The data were digitized

by a Nicolet 1090 AR digital oscilloscope interfaced to a Hewlett Packard 9825A desk computer.

Collection and precision of electrode potentials. Data initially stored in the oscilloscope memory, 0.2 mV/data point, were taken into the computer memory. The computer was programmed to find crossing points for the Q and I components of the second harmonic AC current for E^{rev} measurements and E^Q or the derivative null point for the kinetic potential shift measurements. In general the potentials have a precision of ± 0.5 mV other than in cases, like with AN in the presence of P, where electrode filming is a problem.

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