

# Reactions of Aromatic Anion Radicals and Dianions. VIII.\*

## Reversible Potentials and Spectra of Perylene Anion Radical Undergoing Rapid Chemical Follow-up Reactions

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The measurement of reversible electrode potentials and anion radical visible absorption spectra during the reduction of perylene in dimethylformamide was investigated under conditions where the perylene anion radical was rapidly reacting with acetic acid. Reversible potentials were obtained using cyclic phase selective second harmonic a.c. voltammetry while sine wave modulated specular reflectance measurements were made to obtain spectra of the perylene anion radical. Electron transfer kinetics were shown not to interfere with potential measurements at frequencies as high as 50 kHz. Errors in potential measurements due to uncompensated resistance were eliminated by using very small electrodes. Reversible potential measurements could be obtained under conditions where the pseudo first-order rate constant for the disappearance of the anion radical was about equal to or greater than the frequency at which the measurements were made in accordance with published theory. For example, at 30 Hz it was possible to obtain the reversible potential up to rate constants equal to  $113 \text{ s}^{-1}$  while at 300 Hz the reversible potential was measured under conditions where the rate constant was equal to  $338 \text{ s}^{-1}$ . The most reliable measurement of the reversible potential in cases where the voltammograms do not exhibit identical forward and backward zero crossing potentials was suggested to be the potential halfway between the anodic and cathodic peaks of the backward scan. Anion radical spectra could readily be obtained without signal averaging at rate constants exceeding  $10^3 \text{ s}^{-1}$ .

Reversible electrode potentials for organic redox reactions are useful quantities in kinetic studies of the electrode-generated intermediates. In recent years methods have been developed by this group to measure such potentials for the formation of reactive intermediates by cyclic voltammetry.<sup>1,2</sup> The approach used was to eliminate interfering reactions by the removal of electrophilic or nucleophilic impurities in the solvent-electrolyte systems. The lifetimes of electrode-generated dications<sup>2,3</sup> and dianions<sup>1</sup> could in this way be extended by several orders of magnitude and thus no reactions were observed during the time scale of slow sweep cyclic voltammetry and the resulting cyclic voltammograms could be used to accurately determine the reversible potentials. A shortcoming of this method is that the potentials are often needed for kinetic studies and the assumption must be made that the presence of the second reactant in low concentration does not change the value of the reversible potential. This assumption has been shown to be incorrect in some cases; *i.e.* addition of water or alcohols to dimethylformamide (DMF) solutions of benzophenone<sup>1c</sup> or nitro-substituted aromatic compounds<sup>1c,4</sup> brings about a positive shift of the reversible reduction potential, presumably due to the association of the anionic intermediates and hydroxyl groups by hydrogen bonding.

Smith and coworkers<sup>5,6</sup> have for several years emphasized the advantages of using

\* Parts I—VII, see Ref. 1.

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phase selective second harmonic alternating current voltammetry for the measurement of reversible redox potentials. A recent paper was devoted to a comparison of d.c. and a.c. methods for the measurements in reacting systems and pointed out strong advantages favoring the use of second harmonic a.c. methods.<sup>6</sup> Calculations showed that the potential measured for the formation of reactive intermediates should be that of the reversible electrode reaction even when the pseudo first-order rate constant for the follow-up reaction was as high as  $10^3 \text{ s}^{-1}$ . Experimental work reported in connection with the use of phase selective second harmonic measurements in reacting systems was restricted to rather slow chemical follow-up reactions, the fastest case having a pseudo first-order rate constant of about  $10 \text{ s}^{-1}$ .<sup>6</sup>

The object of this paper is to verify the predictions of Smith regarding the measurement of reversible potentials for the formation of rapidly reacting intermediates and to report complimentary data for the same systems from sine wave modulated specular reflectance measurements.

## EXPERIMENTAL

*Reagents, electrodes, and cells.* Reagent grade perylene was used without further purification. DMF was distilled under vacuum from cupric sulfate before use. Tetrabutylammonium fluoroborate was prepared by ion exchange from the hydrogen sulfate (Hässel, Gothenburg), precipitated from dichloromethane with ether and dried. The working electrodes for voltammetric measurements were prepared by sealing small diameter platinum wire in glass and polishing to a planar surface as previously described.<sup>7</sup> Reference electrodes were Ag/AgNO<sub>3</sub> (0.1 M) in acetonitrile constructed in the manner described by Moe.<sup>8</sup> 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 accommodate a teflon electrode holder equipped with a tube for the inlet of purified nitrogen. The cell used for spectroelectrochemical measurements was similar to that described by Bewick.<sup>9</sup>

*Instrumentation.* The potentiostat was a PAR model 173D driven by a PAR 175 function generator. The a.c. signal source was a PAR 189 oscillator and the phase sensitive detector was a PAR 129A lock-in amplifier. Voltammograms, (a.c. amplitude = 20 mVrms; d.c. sweep rate = 20 mV/s), were recorded on a Hewlett Packard

XYY recorder model 7046A. The amplification on the X (voltage) axis was 25 mV/cm and the potential measurements, the second harmonic crossing points ( $E^c$ )<sup>6</sup> were accurate to  $\pm 0.002 \text{ V}$ .

The same instrumentation was used for the modulated specular reflectance measurements along with a Harrick RSS-B rapid scanning spectrometer.

## RESULTS AND DISCUSSION

In order to assess the effect of follow-up chemical reactions on the measurement of reversible potentials for an electrode process it is first necessary to establish the reversibility of the electrode reaction under the conditions of the measurements. The theoretical predictions concerning the use of the second harmonic crossing potential ( $E^c$ ) for reversible potential measurements assume fast electron transfer.<sup>6,10</sup> In order to assure that the reduction of perylene in DMF fits the criteria for reversibility over the frequency range studied, phase selective second harmonic voltammograms were recorded at frequencies up to 50 kHz. Voltammograms recorded at 300, 3 000, and 30 000 Hz are shown in Fig. 1. The voltammograms were obtained using a platinum electrode constructed from wire of diameter equal to 0.03 mm as described in the experimental section. The point of interest is that the cross-over potentials  $E_1^c$  and  $E_2^c$ , as well as the peak potentials were found to be independent of the frequency over the range studied. Attempts to use larger electrodes for the experiments were less successful presumably due to the increased demands upon the potentiostat to handle larger double-layer charging currents at the high frequencies. The voltammograms show that both the first and second electron transfers to perylene are fast relative to the a.c. frequencies used in the measurements.

The measurements shown in Fig. 1 were made under conditions where the products of both electron transfers, the perylene anion radical and the dianion are stable. Theoretical calculations have been presented<sup>10,11</sup> which predict that the phase selective zero current point,  $E^c$ , occurs precisely at  $E^x$ , the reversible potential when  $k/\omega < 3$  where  $k$  is the first-order or pseudo first-order rate constant for the disappearance of the electrode-generated intermediate and  $\omega$  is the angular frequency. From these calculations, one would predict that the reversible potential could be measured at 30 kHz under con-

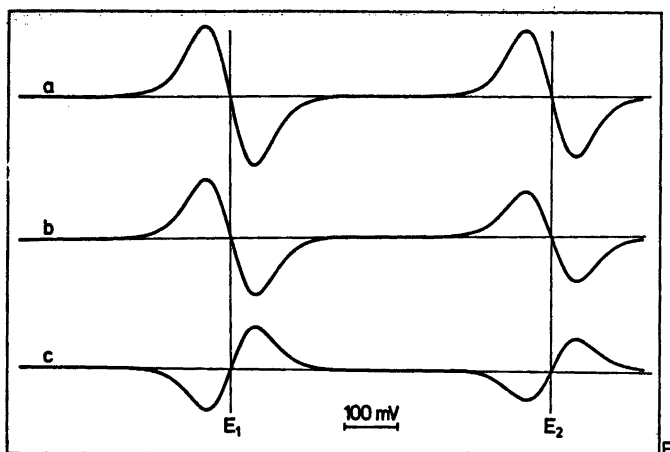


Fig. 1. Phase selective second harmonic a.c. voltammograms for the two consecutive one electron reductions of perylene in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.2 M); frequency equal to (a) 300 Hz, (b) 3000 Hz, and (c) 30 000 Hz.

ditions where  $k$  is equal to or less than about  $10^5 \text{ s}^{-1}$ .

We have recently been studying the protonation reactions of perylene anion radicals with moderately strong proton donors such as acetic and even stronger carboxylic acids.<sup>12</sup> These systems appeared to be ideal test cases for the theoretical calculations of the applicability of phase selective second harmonic voltammetry<sup>5,6,10,11</sup> for the measurement of reversible

Table 1. Reversible electrode potentials for the reduction of perylene in DMF.<sup>a</sup>

[HOAc]/M	$-(E^c)_f^b$	$-(E^c)_b^b$	$k/\text{s}^{-1}^c$
0	1.983	1.983	0
0.029	1.983	1.983	5.8
0.058	1.983	1.983	11.6
0.087	1.983	1.983	17.4
0.116	1.983	1.980	23.2
0.230	1.985	1.890	46.0
0.343	1.987	1.985	68.6
0.455	1.990	1.985	91.0
0.565	1.998	1.988	113

<sup>a</sup> Measured at 30 Hz, d.c. sweep rate  $20 \text{ mVs}^{-1}$ , supporting electrolyte was  $\text{Bu}_4\text{NBF}_4$  (0.2 M), [perylene] = 1.0 mM, potentials in V. <sup>b</sup> Subscripts refer to the forward and backward scan, respectively. <sup>c</sup> Pseudo first-order rate constant for the disappearance of the anion radical calculated from data in Ref. 12.

potentials in rapidly reacting redox systems since the value of  $k$  could be varied by simply increasing the concentration of the proton donor.

Data for the potential measurements for the reduction of perylene in DMF under conditions where the perylene anion radical was undergoing reaction with acetic acid are summarized in Tables 1 and 2. Measurements were made under cyclic conditions<sup>13</sup> so that  $E^c$  could be evaluated both on the forward and the backward potential scan. The data recorded at a frequency of 30 Hz clearly show that the  $E^c$  values in both directions are constant within experimental error until [HOAc] greater than about 0.3 M are encountered above which  $(E^c)_f$  begins to increase. The value of  $(E^c)_b$ , i.e. the measurement from the backward scan does not deviate until a slight increase is observed in the final entry at [HOAc] equal to 0.565 M. The pseudo first-order rate constants for the disappearance of the anion radical<sup>12</sup> are summarized in the final column. The last two entries equal or exceed the value of  $3\omega$ . We can consider the data obtained at 300 Hz before commenting on the differences observed in  $(E^c)_f$  and  $(E^c)_b$ .

Cyclic phase selective second harmonic voltammograms measured at 300 Hz for the reduction of perylene in DMF containing acetic acid, 0.565 M (a), 1.094 M (b) and 1.591 M (c), are illustrated in Fig. 2. At the lowest acid concentration, both the forward scan and the

**Table 2.** Comparison of methods of measurement of reversible potentials for the reduction of perylene in DMF.<sup>a</sup>

[HOAc]/M	$-(E^c)_f^b$	$-(E^c)_b^b$	$-E_{ci}^c$	$-(E^{\ddagger})_b^d$	$k/s^{-1}^e$
0.565	1.983	1.983	1.983	1.975	113
0.673	1.983	1.983	1.983	1.975	135
0.780	1.988	1.985	1.989	1.978	156
0.886	1.988	1.985	1.990	1.975	177
0.991	1.990	1.985	1.998	1.978	198
1.094	1.993	1.988	1.999	1.978	219
1.196	1.985	1.989	2.000	1.973	239
1.296	1.990	1.989	1.983	1.975	260
1.396	1.998	—	1.980	1.978	280
1.494	1.993	—	1.983	1.978	298
1.591	2.000	—	1.978	1.975	318
1.687	2.005	—	1.979	1.975	338

<sup>a</sup> Measured at 300 Hz, d.c. sweep rate 20 mV s<sup>-1</sup>, supporting electrolyte was Bu<sub>4</sub>NFB<sub>4</sub> [0.2 M], [perylene] = 1.0 mM, potentials in volts. <sup>b</sup> Second harmonic zero current potential, subscripts refer to the forward and backward scan, respectively. <sup>c</sup> The potential where the second harmonic a.c. forward and backward scans intercept each other. <sup>d</sup> The potential half way between the oxidation and reduction peaks of the second harmonic a.c. voltammogram on the backward scan. <sup>e</sup> Pseudo first-order rate constant for the disappearance of the anion radical calculated from data in Ref. 12.

reverse scan exhibit zero current crossing points,  $(E^c)_f$  and  $(E^c)_b$ , at -1.983 V which is the same value obtained in the absence of acetic acid. The traces of the forward and backward scans are unsymmetrical, the reduction peak currents being greater than the oxidation peak currents. This asymmetry is due to the rapid follow-up reaction of the anion radical.<sup>11</sup> The asymmetry is much less pronounced on the backward trace, a fact which we will use later in the discussion.

At higher acetic acid concentrations (b) we see that the forward and backward traces no longer intercept the zero current axis at the same potential but intercept each other in the anodic current region. At still higher acid concentrations (c) only the forward trace intercepts the zero current line, while the backward trace, still retaining its nearly symmetrical shape, falls entirely in the cathodic current region.

**Table 3.** Effect of rapid chemical follow-up reactions on modulated specular reflectance absorbance of the perylene anion radical.

[HOAc]/M	Modulating frequency (Hz)					$k^b/s^{-1}$
	Values of absorbance (Relative) <sup>a</sup>					
	3	10	30	60	80	
0.035	18.3	11.6	7.15	4.9	4.4	7.0
0.052	16.8	10.1	6.0	4.25	3.65	10.4
0.070	14.6	8.8	5.2	3.65	3.2	14.0
0.087	13.5	8.35	4.9	3.5	3.05	17.4
0.104	12.4	7.3	4.35	3.1	2.75	20.8
0.139	9.6	6.1	3.6	2.75	2.3	27.8
0.173	7.3	5.1	3.2	2.3	2.0	34.6
0.343	2.7	3.0	2.0	1.65	1.45	68.6
0.510	—	1.65	1.4	1.2	1.0	102

<sup>a</sup> Values at absorbance maximum (582 nm) for the perylene anion radical in DMF. Phase sensitive detection with sine wave modulation with an amplitude of 200 mV about  $E_{rev}$  during reduction of perylene. <sup>b</sup> Pseudo first-order rate constant for the disappearance of the anion radical based on a second-order rate constant of 200 M<sup>-1</sup> s<sup>-1</sup> from Ref. 12.

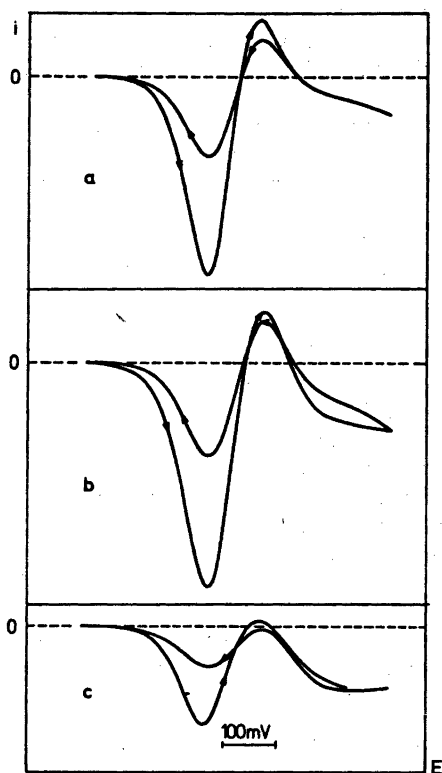


Fig. 2. Phase selective cyclic second harmonic voltammograms of perylene in DMF, (HOAc) = 0.565 M (a), 1.094 M (b) and 1.591 M (c).

Second harmonic zero current crossing potentials on forward and backward traces should be identical. The fact that those shown in Fig. 2 are not indicates a complication due to a shift in background currents or base line in the forward and backward scans. Obviously, this brings about uncertainty as to which potential to use as the reversible value. Several different measures of the reversible potential are given in Table 2 for the reduction of perylene in DMF containing varying amounts of acetic acid measured at 300 Hz. The forward and backward crossing potentials have already been defined. The symbol  $E_{ci}$  indicates the potential at which the forward and backward traces intercept each other and  $(E^{\ddagger})_b$  is the potential half way between the oxidation and reduction peaks of the nearly symmetrical backward trace. The rate constants given in the table are those calculated for the pseudo first-order reaction of the

perylene anion radical. Measurements were made under conditions where  $k$  was as great as  $338 \text{ s}^{-1}$ . At higher values of  $k$ , i.e. greater concentrations of HOAc, the deformation of the voltammograms became more serious and neither a forward nor backward crossing point was observed. A possible reason for the deformation and the non-identity of the forward and backward zero current crossing potentials is that the reduction of acetic acid or some other complicating electrode reaction is beginning to interfere.\*

There are some interesting aspects of the data in Table 2. The forward crossing potential appears to be less reliable than that of the backward trace. An error of the order of 20 mV in the value of the reversible potential would be made if  $(E^c)_f$  was used at the highest acid concentration. On the other hand  $(E^c)_b$  gives a reliable estimate of the reversible potential in all cases that it is observed with a maximum error of the order of only 6 mV. The point where the forward and backward traces intercept,  $E_{ci}$ , is the poorest estimate of the reversible potential from the data given in Table 2 and thus there is no advantage to its use. The quantity which gives the most constant value throughout Table 2 is  $(E^{\ddagger})_b$  as defined above. Returning our attention to Fig. 2c, we note that even at the very high acid concentration that the near symmetry of the backward wave is retained. This suggests that this segment of the voltammogram should be of use in measuring the reversible potential. But as noted before, no zero current crossing point is observed. However, in the absence of complications the symmetrical phase selective second harmonic voltammogram crosses the zero current axis at a potential halfway between the anodic and cathodic peaks and this is the reversible potential. Knowing that a complication does exist which does not allow the backward trace to pass through the zero current axis seems to justify taking the potential halfway between the anodic and cathodic peaks on a symmetrical second harmonic voltammogram as the reversible potential. Returning to the data in Table 2 we see that the average values of  $(E^{\ddagger})_b$  is equal to  $-1.976 \pm 0.002 \text{ V}$  and that all of the values

\* The d.c. background current becomes significant at about 0.5 V in the presence of acetic acid.

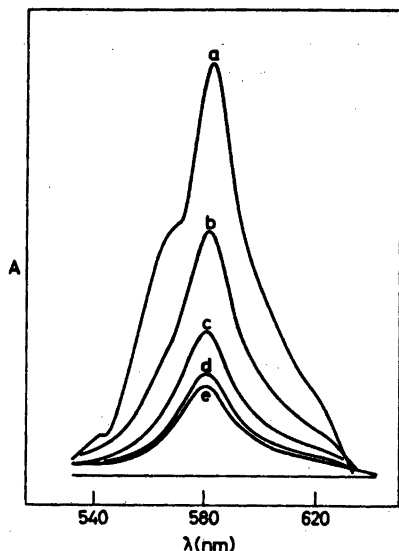


Fig. 3. Visible absorption spectra of the perylene anion radical in DMF containing acetic acid (70 mM), measured by modulated specular reflectance at 3 Hz (a), 10 Hz (b), 30 Hz (c), 60 Hz (d) and 80 Hz (e).

listed with the exception of one ( $-1.973$ ) fall in this range. This value differs by 7 mV from the reversible potential in the no reaction case,  $-1.983$  V. The reason for the discrepancy is obvious from Fig. 2a under which conditions  $(E^c)_f$  and  $(E^c)_b$  cross the zero current axis at the same potential which defines the reversible potential. We can see that the backward scan is not symmetric about zero current and this asymmetry is responsible for the difference between  $(E^c)_b$  and  $E^{rev}$ . However, we conclude that when the forward and backward crossing potentials are not the same and the backward trace of the cyclic phase selective second harmonic voltammogram is symmetrical or nearly so as in the present case, that  $(E^c)_b$  is the most reliable estimate of the reversible potential. Furthermore, in most organic redox systems complications are observed and identical forward and backward zero current crossing potentials probably will not be observed.

Modulated electrochemical specular reflectance<sup>9,14</sup> measurements have many features in common with a.c. voltammetry and are very useful in characterizing intermediates of fast follow-up reactions.<sup>15</sup> The data in Table 3 were

obtained under conditions comparable to the reversible potential measurements. Sine wave modulation of the potential with an amplitude of 200 mV either side of  $E^{rev}$  for the reduction of perylene in DMF at different frequencies and acetic acid concentrations resulted in spectra of the perylene anion radical. Relative absorbances are listed in Table 3 for the maximum at 582 nm. Even at the lowest frequency, 3 Hz, it was possible to obtain a spectrum under conditions where the rate constant for the reaction of the anion radical with acetic acid was equal to  $68.6$  s<sup>-1</sup>. At the higher frequencies, spectra were obtained in cases where the rate constant was as high as  $102$  s<sup>-1</sup>. This is by no means the limit since signal averaging of the spectra<sup>16</sup> would allow much smaller absorbances to be measured. The data show that low frequencies give more intense spectra in slowly reacting systems but as the reaction rate increases it is necessary to go to higher frequency to obtain spectra. The spectra are illustrated in Fig. 3. Calculations on the frequency dependence of spectra in rapidly reacting redox systems will appear later.<sup>17</sup>

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