

## PROPERTIES OF AROMATIC IONS GENERATED AT ELECTRODES

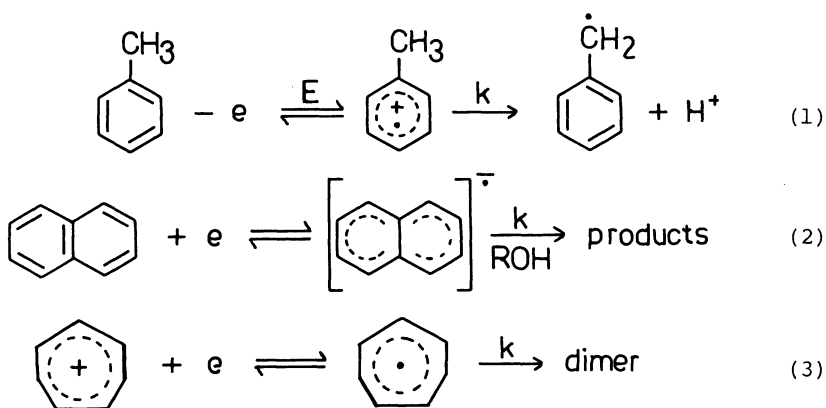
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**Abstract** - The methods for the measurement of reversible electrode potentials for the formation of rapidly reacting organic ions and radicals are discussed. Second harmonic ac voltammetry gives the most accurate results. Reliable estimates can be made even when the rate of the follow-up reaction precludes the direct measurement. An analysis of the probable error due to the effect of the kinetic step is made. The measurement of rate constants of several representative reactions, the rates of which are too great to be determined by most other electrochemical techniques, have been carried out using potentials measured by second harmonic ac voltammetry. The method is based upon an empirically derived linear relationship between the measured potential and the rate constant for the follow-up reaction. Examples of electron transfer reactions producing intermediates differing substantially in conformation from that of the substrate are discussed.

### INTRODUCTION

Electrochemical techniques are especially well suited for the study of the formation and reactions of organic ions and radicals. The aromatic compounds and their ions are the most readily studied due to the ease with which they undergo electron transfer reactions. The measurements yield both thermodynamic and kinetic data. Examples of types of reactions coupled to electron transfer at an electrode which can be studied are illustrated in eqns. (1-3). The data which we can attempt to obtain for such reactions are (a) the reversible or thermodynamic potentials for the electron transfer reactions and (b) the rate constants for the reactions following charge transfer.



### APPLICATIONS OF ELECTRODE POTENTIAL DATA

One of the most frequently exploited aspects of the electrode potentials for the oxidation and reduction of aromatic compounds is the relationship to the gas phase energies for the redox processes. Correlation of voltammetric data

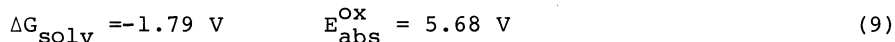
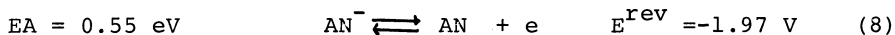
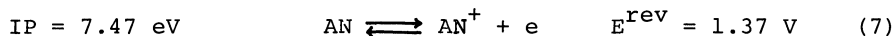
with ionization potentials and electron affinities has firmly established that the solution and gas phase energetics are related and to the first approximation, linearly (Refs. 1-5). A recent application of these ideas has led to the proposal of an "absolute" electrode potential scale (Ref. 6). The basis for this proposal is the measurement of reversible potentials for both the oxidation and reduction of large alternant aromatic hydrocarbons such as anthracene. The primary assumption involved is that the size, shape, and degree of charge dispersal of the anion and cation radicals are identical or nearly so, and thus the solvation energies of the ions should be the same. This same assumption had previously been made in the estimation of solvent surface potentials (Ref. 7). Neglecting gas phase entropy effects and solvent surface potentials, which are expected to be small, led to eqns. (4) and (5) for the "absolute" potentials for oxidation and reduction, respectively, of a compound. If the potentials for both processes can be measured in the same solution, then the difference in potential, which is independent of the reference scale, is given by eqn. (6).

$$E_{\text{abs}}^{\text{ox}} = \text{IP} + (\Delta G_{\text{solv}})^{\text{cation}} \quad (4)$$

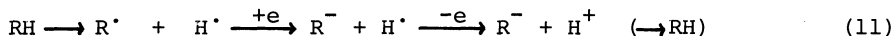
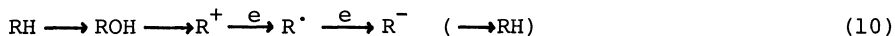
$$E_{\text{abs}}^{\text{red}} = \text{EA} - (\Delta G_{\text{solv}})^{\text{anion}} \quad (5)$$

$$\Delta E^{\text{ox-red}} = \text{IP} - \text{EA} + (\Delta G_{\text{solv}})^{\text{cation}} + (\Delta G_{\text{solv}})^{\text{anion}} \quad (6)$$

Application of the latter equation, assuming the equality of the solvation energies of the positive and negative ions, resulted in a value for the solvation energy ( $\Delta G_{\text{solv}}$ ) and hence the "absolute" potentials for the oxidation and reduction processes. The method is illustrated for anthracene (eqns. 7-9) in acetonitrile using literature values for the ionization potential (Ref. 8) and electron affinity (Ref. 9). The potential for any other electrode process can be placed on this "absolute" scale by reference to the potentials for anthracene (Ref. 10).

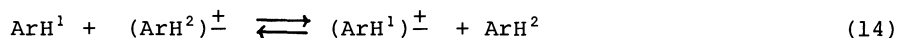
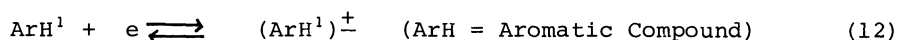


Electrode potentials have been used by Breslow and coworkers to estimate the acidities of a number of weakly acidic hydrocarbons (Refs. 11-16). The method employs one or the other of the thermodynamic cycles illustrated by eqns. (10-11).



The bond dissociation energies involved are either known or can be estimated. Electrode potential data then complete the energetics of the cycles and give the  $\text{pK}_a$  values. Representative  $\text{pK}_a$  data obtained in this manner include: triphenylmethane (31.5), propene (53), toluene (54), propyne (63) and isobutane (71).

Another application is the determination of equilibrium constants for electron transfer reactions. Potentials are measured for half-reactions (12) and (13) and the Nernst equation is then employed to give the equilibrium constant for reaction (14). Potentiometric titration was used by Hoijsink (Ref. 17) and Szwarc (Ref. 18) to determine equilibrium constants for electron exchange reactions between aromatic compounds and anion radicals while Svanholm and Parker (Ref. 19) obtained the  $K$  values for cation radical reactions from cyclic voltammetric data. A special case is the disproportionation reactions of aromatic anion and cation radicals which have been discussed a great deal in connection with the mechanisms of the ion radical reactions. Representative data for both anion radicals (Ref. 20) and cation radicals (Ref. 21) determined



$$\ln K = (F/RT)(E_{12} \pm E_{13}) \quad (15)$$

by cyclic voltammetry are given in Table 1.

TABLE 1. Disproportionation equilibrium constants of ion radicals

Ion radical	$\Delta E/\text{mV}$	K
Perylene anion radical	615	$1 \times 10^{-11}$
Anthracene anion radical	740	$7 \times 10^{-14}$
Thianthrene cation radical	510	$2 \times 10^{-9}$
4,4'-Dimethoxybiphenyl cation radical	270	$3 \times 10^{-5}$

#### MEASUREMENT OF REVERSIBLE ELECTRODE POTENTIALS

When an electron exchange reaction between an electrode and a substance in solution is fast relative to the measurement technique and both species of the redox couple are stable in solution the electron transfer is considered reversible and the potential measured is called the reversible potential. Such potentials have thermodynamic significance and can be used for the applications described in the preceding section. The majority of organic ions and radicals generated at electrodes are not stable and undergo reactions at finite rates during the measurement of the potentials. If the reactions are sufficiently fast, the measured potential will be less negative for a reduction and less positive for an oxidation than the corresponding reversible potential. Such kinetic shifts were discussed in detail by Nicholson and Shain (Ref. 22) for cyclic voltammetry in 1964 and have been investigated by a number of workers since then using various electroanalytical methods. At 25° the difference in measured and reversible potentials,  $\Delta E^P$ , for linear sweep voltammetry is given by equation (16) for a first order reaction following electron

$$\Delta E^P = 0.0085 + 0.059 \log \sqrt{k/a} \quad (16)$$

transfer where  $k$  is the rate constant and  $a$  is equal to  $Fv/RT$  and  $v$  is the voltage sweep rate in  $\text{Vs}^{-1}$ . For example when  $k$  is equal to  $10^7 \text{ s}^{-1}$  and the voltage sweep rate is  $100 \text{ mVs}^{-1}$   $\Delta E^P$  is predicted by eqn. (16) to be equal to about 220 mV, a significant error in the measured potential.

The most common technique for determining electrode potentials is cyclic voltammetry. The potential region of interest is traversed from a potential where no current flows to a potential beyond where the electron transfer reaction becomes diffusion controlled and then back to the original starting point using a triangular potential-time wave form. A cyclic voltammogram for a reversible one electron transfer is shown in Fig. 1a. The features of interest are that the peak to peak potential separation is equal to 58 mV at 25° and the ratio of peak currents on the forward and backward scans is equal to unity. The voltammogram takes the form of Fig. 1b when a rapid chemical reaction accompanies the charge transfer.

The reaction of the electrode-generated intermediate with impurities in the reaction medium has been found to be a major cause for the failure to observe reversible cyclic voltammograms for many electrode processes involving aromatic compounds (Refs. 20,21,23-25). A simple technique was developed which effectively removes all nucleophilic and electrophilic impurities from solvent-supporting electrolyte systems. It was found that reversible potentials could be obtained by cyclic voltammetry for such reactive species as aromatic

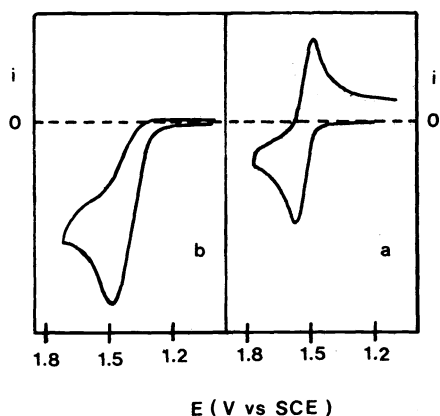


Fig. 1. Cyclic voltammograms showing a reversible electron transfer (a) and the effect of a rapid chemical follow-up reaction (b).

dications (Ref. 21) and dianions (Ref. 23) simply by carrying out the voltammetric measurements with neutral alumina in the cell. It was later shown that the same effect could be achieved by cycling the voltammetric solution through a column of alumina and the cell several times under vacuum (Ref. 26). A cyclic voltammogram typical for the oxidation or reduction of aromatic compounds using the alumina technique is illustrated in Fig. 2.

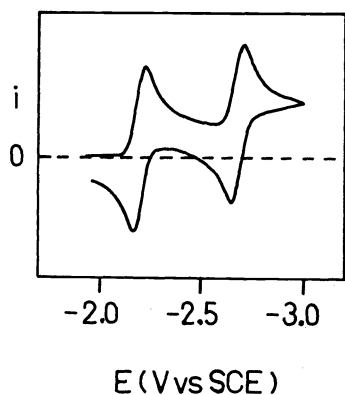


Fig. 2. Cyclic voltammogram for the two step reduction of trans-stilbene in DMF in the presence of neutral alumina.

Another way of suppressing a reaction following charge transfer is to add a reagent to reverse the reaction. It was demonstrated that the reversible potentials for the oxidation of a number of phenols, the cation radicals of which undergo very rapid deprotonation, could be obtained in dichloromethane saturated with fluorosulfonic acid. The effect of the acid was to make deprotonation less favorable (Ref. 27).

An undesirable feature of obtaining reversible potentials by suppressing follow-up reactions is that the potentials may not be the same as those which apply under conditions where reactions are taking place. For example, it has been observed that the reversible potential for the formation of the dianion of *p*-dinitrobenzene in dimethylformamide is dependent upon the presence of hydroxylic compounds (Refs. 28-29). The difference in reversible potentials for the first and second charge transfer to the parent compound was found to vary from 650 mV in the absence of methanol to approximately zero when the methanol concentration was about 7 M. The second charge transfer to benzophenone was found to be even more sensitive to the presence of low concentrations of hydroxylic compounds (Ref. 28). Thus, when electrode potential data are used in regard to mechanisms of reactions of electrode generated intermediates, the reversible potentials should be those that prevail under

conditions where the reaction is taking place. The presence of other reactants may bring about significant shifts in the thermodynamic potentials.

Second harmonic ac voltammetry is the method of choice for the measurement of reversible potentials in systems where the electro-generated intermediate is reacting at moderately high rates. For the case of an irreversible reaction following charge transfer (eqn. 17) Smith (Ref. 30) has carried out calculations which indicate that reversible potentials can be measured, providing



that charge transfer is fast, as long as the first order rate constant  $k$  does not exceed  $3\omega$  where  $\omega$  is the angular frequency of the applied ac voltage. This indicates that in many cases reversible potential measurements should be possible up to  $k$  values of about  $10^4 \text{ s}^{-1}$ . The second harmonic voltammograms measured for a reversible system, eqn. (17)  $k=0$ , are shown in Fig. 3. Traces of the  $I$  (in phase) and  $Q$  (quadrature,  $90^\circ$  out of phase) components of the

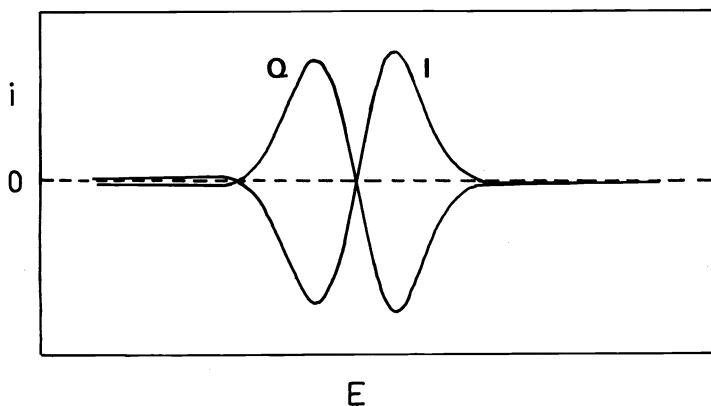


Fig. 3. The in phase and quadrature components of the second harmonic ac current for a reversible electron transfer.

second harmonic ac current exhibit current peaks of equal magnitude and intersect at the zero current line. This is a consequence of the fact that the fundamental ac current leads the applied potential by  $45^\circ$  and has a maximum value at  $E^{rev}$  while the  $I$  and  $Q$  components of the second harmonic ac current are  $45^\circ$  out of phase with, on either side of the latter. The symmetric shape of the  $I$  and  $Q$  voltammograms is only observed when  $\omega$  is very much larger than

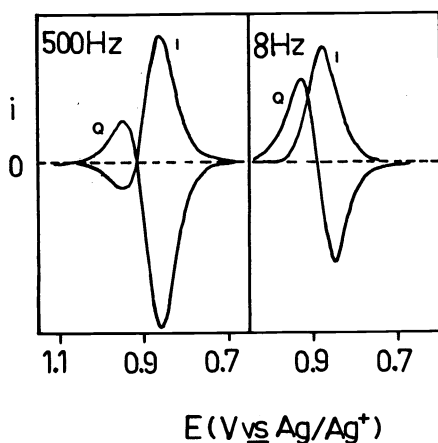


Fig. 4.  $I$  and  $Q$  components of the second harmonic ac current during the oxidation of DPA in acetonitrile in the presence of pyridine measured at 8 and 500 Hz.

k. When  $k$  becomes significantly large, the symmetry disappears but the I and Q traces still intersect at zero current as long as  $\omega$  is sufficiently large, *i.e.* greater than  $k/3$  according to the calculations.

Voltammograms for a reacting system, 9,10-diphenylanthracene (DPA) cation radical with pyridine under conditions where the pseudo first order rate constant for eqn. (17) is equal to  $84 \text{ s}^{-1}$ , are illustrated in Fig. 4. At 8 Hz the Q component appears as a nearly symmetrical trace while the I component voltammogram does not cross the zero current line. The measurement made at 500 Hz illustrates both the unsymmetrical nature of the I and Q traces as well as the zero current crossing point. Thus, reversible potentials are obtained as long as the I and Q components intersect at zero current (Ref. 31) and the symmetric relationship only holds for the no reaction case. The frequency required to "outrun" the follow-up reaction is somewhat disappointing in terms of the theoretical predictions. Theory (Ref. 30) predicts that an angular frequency  $\omega$  equal to  $k/3$  or in this case  $28 \text{ s}^{-1}$  should be adequate to observe the reversible potential. This corresponds to an applied frequency  $f$  of about 4.5 Hz ( $\omega = 2\pi f$ ). Although the 8 Hz experiment was expected to yield the reversible potential, an applied frequency of nearly 100 times as great as predicted was required.

There is some confusion in the literature regarding the symmetry of reversible second harmonic ac voltammograms. Reversible potentials, taken from symmetric or nearly symmetric second harmonic ac voltammograms, have been reported for a number of rapidly reacting redox systems (Ref. 13). The latter is inconsistent with the discussion above. An example is the reduction potential for the tropylium cation, which was measured at 45 Hz, under conditions where the radical was undergoing rapid dimerization according to eqn. (3). Voltammograms measured at 45 Hz in our laboratory are illustrated in Fig. 5. The I and Q

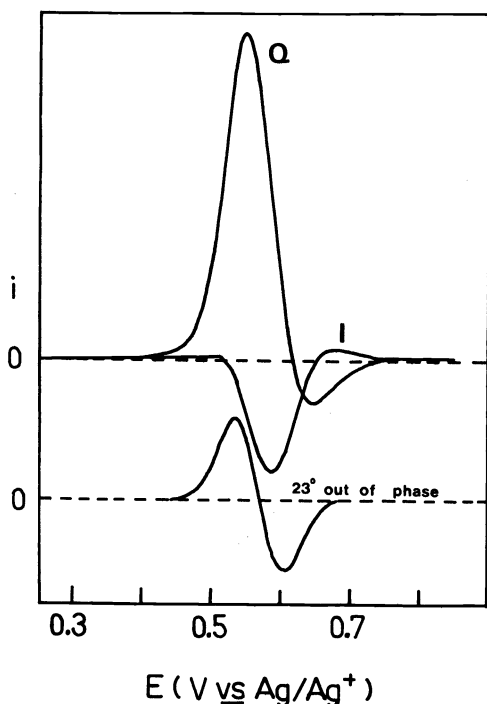


Fig. 5. I, Q, and  $23^\circ$  out of phase components of the second harmonic ac current during the reduction of tropylium cation in acetonitrile.

components are decidedly asymmetric and do not intersect at the zero current line. The symmetric voltammogram in the lower part of the figure was obtained by shifting the phase  $23^\circ$  and crossed the zero current axis about 60 mV positive of the point of intersection of the I and Q components. It is clear that symmetry cannot be used as an indication of reversibility and that the observation of either a symmetric I or Q component for a rapidly reacting redox system must be regarded with suspicion. Exact values of reversible potentials

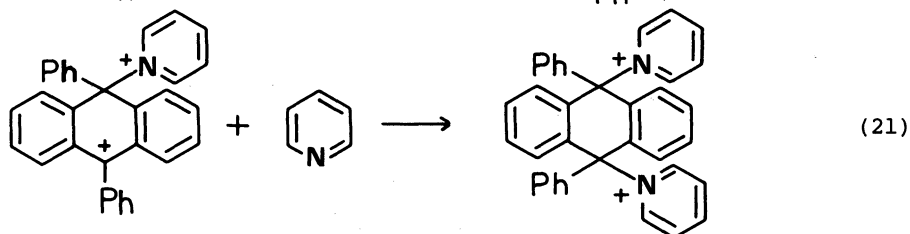
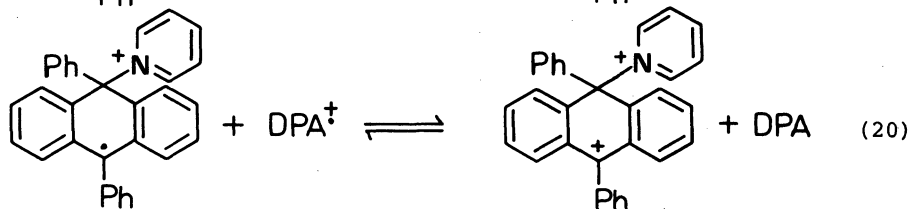
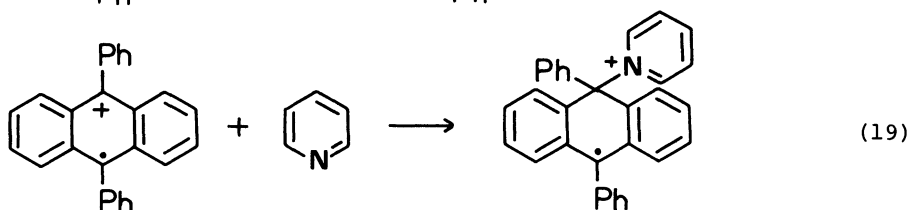
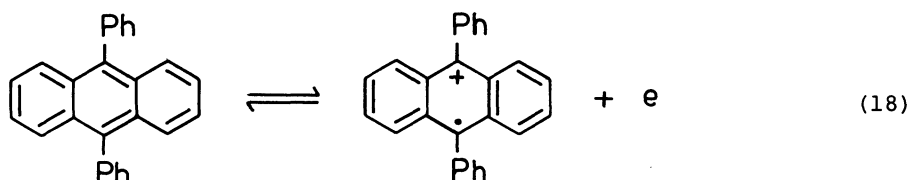
can only be assigned when the I and Q components give traces intersecting at zero current.

It is often found that the presence of electrophiles or nucleophiles during the generation of aromatic anions or cations is accompanied by reduction or oxidation currents which make the measurement of reversible potentials difficult. Such effects are minimized by using ac voltammetry because the ac current flows over a relatively narrow potential region for a given electrode process. Despite this, the background current can still interfere with the measurement of reversible potentials as was observed for the reduction of perylene in the presence of acetic acid (Ref. 32). However, reliable estimates of the reversible potentials were obtained by second harmonic ac voltammetry using cyclic (Ref. 33) conditions in cases where the pseudo first order rate constants were as great as about  $300 \text{ s}^{-1}$  (Ref. 32).

Although applications to reacting organic systems are limited the technique of second harmonic ac voltammetry shows promise of becoming a very important tool for the measurement of reversible potentials in these systems.

#### KINETICS OF RAPID REACTIONS FOLLOWING ELECTRON TRANSFER

A number of electroanalytical techniques exist for the determination of the rate constants of reactions following charge transfer at an electrode. For reactions of the type illustrated by eqn. (17), the practical limit for the direct determination of  $k$  by most of the techniques is of the order of  $10^4 \text{ s}^{-1}$  (Ref. 34). Many of the reactions of ion radicals and most of those of the doubly charged ions take place at higher rates and are thus out of the practical range for kinetic studies. In principle, the kinetic shift during linear sweep voltammetry should yield the rate constant by application of eqn. (16) for these fast reactions as long as charge transfer is fast and the reversible potentials are known.



The reaction of DPA cation radical with pyridine was used as a test system to determine the reliability of using linear sweep voltammetry for the determination of rate constants of fast reactions following charge transfer at an electrode. The oxidation of DPA in acetonitrile in the presence of pyridine is accompanied by the reactions shown in eqns. (18-21). The rate constant for reaction (19) has been determined by a number of techniques including rotating disc electrode voltammetry (Ref. 35), spectroelectrochemistry (Ref. 36) and homogeneous kinetics (Ref. 37). The rate constant for the reaction in acetonitrile at room temperature is equal to  $2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ . Potential shifts from the reversible value as a function of pyridine concentration for the reaction in acetonitrile are summarized in Table 2 where the peak potential shifts were measured at a voltage sweep rate equal to  $100 \text{ mVs}^{-1}$  (Ref. 38). The calculated second order rate constants were observed to be nearly independent of the pyridine concentration but an order of magnitude lower than the known value (see Note a).

TABLE 2. Second order rate constants determined by peak voltammetry.

[pyridine]/M	$\Delta E^D/\text{mV}$	$\log(k_{\text{calc}}/\text{s}^{-1})$	$\log(k_{\text{calc}}/\text{M}^{-1}\text{s}^{-1})$
0.0042	22.5	1.065	3.44
0.0084	32.5	1.404	3.48
0.0211	42.5	1.743	3.42
0.0422	51	2.031	3.41
0.0844	60	2.336	3.41

The fact that the second order rate constants calculated using eqn. (16) did not vary significantly while the pseudo first order rate constant was being varied by a factor of 20 showed that the calculations give correct relative but not absolute values of the rate constants using the linear sweep method. The latter suggested that a calibration using reactions with known rate constants could make the method suitable for the determination of reliable rate constants. However, the use of dc peak potentials has two disadvantages which seriously impair the method. The first is the accuracy. The exact potential at which the peak occurs on a linear sweep voltammogram is experimentally difficult to determine and accuracy better than 5 mV cannot be expected. Secondly, it is not possible to measure a dc peak potential for the oxidation or reduction of an ion radical which is undergoing rapid reaction. Thus, in cases where the ion radicals are reacting, it is not possible to study the kinetics of the reactions of the dianions or dications by peak voltammetry.

In order to avoid the difficulties discussed above, second harmonic ac voltammetry was adopted to obtain rate constants from kinetic potential shifts (Ref. 38). As shown in the discussion of the voltammetry of the tropylium cation, the symmetric shape of a second harmonic ac voltammogram can be achieved by a phase adjustment. The zero current crossing potential taken from a symmetric trace, although not equal to  $E^{\text{rev}}$ , can easily be measured with an accuracy of 1 mV and the potentials for dianion and dication formation can be measured even when the ion radicals are undergoing rapid reaction.

The system chosen for the calibration of the method was the reaction of DPA cation radical with pyridine. The second harmonic zero current crossing potentials ( $E^C$ ) measured at 8 Hz (Fig. 4) were observed to vary linearly with the pyridine concentration during the oxidation of DPA in acetonitrile containing pyridine. The slopes and intercepts for plots of  $\log k$  vs.  $\Delta E^C$ , where

Note a. Equation (16) was derived for the EC reaction while reactions (18-21) follow an ECC scheme. Calculations show that only minor differences are predicted for the two mechanisms in terms of the peak potential shift.



$k$  is the pseudo first order rate constant for reaction (19) and  $\Delta E^C$  is the difference between the reversible potential and the potential measured at 8 Hz under the reaction conditions, were averaged for four independent sets of experiments in which  $k$  was varied over a factor of 20 by adjusting the pyridine concentration. This procedure resulted in eqn. (22) to relate the rate constant with the measured potential (Ref. 38). Further work, including measurements on much faster reactions with known rate constants, is necessary to complete the calibration procedure.

$$\log k = 0.06 \Delta E^C + 0.6 \quad (22)$$

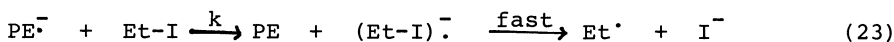
Equation (22) was used to determine the second order rate constant for the reaction between perylene anion radical and oxalic acid, a reaction which had previously been studied using double step chronoamperometry and a rate constant of about  $10^4 \text{ M}^{-1}\text{s}^{-1}$  was assigned (Ref. 39). These data are gathered in Table 3.

TABLE 3. Rate constants for the reaction between perylene anion radical and oxalic acid in DMF at 20°.

$[\text{HO}_2\text{CCO}_2\text{H}]/\text{M}$	$\Delta E^C/\text{mV}$	$\log(k/\text{s}^{-1})$	$\log(k_2/\text{M}^{-1}\text{s}^{-1})$
0.0074	25	2.10	4.23
0.0148	30	2.40	4.23
0.0296	32.5	2.55	4.08
0.0741	40	3.00	4.13
			ave. 4.17

The fact that the second order rate constants given in Table 3 are very nearly independent of the oxalic acid concentration verifies the linear relationship as well as the value of the slope, *i.e.* 0.06 in eqn. (22). The rate constants are in good agreement with those obtained by double step chronoamperometry (Ref. 39).

The reactions between anion radicals and alkyl halides have been actively investigated (Refs. 40-41). These reactions are normally assigned an electron transfer mechanism as in eqn. (23). Kinetic potential shift data were obtained



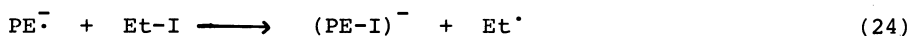
for the reaction between the perylene anion radical and ethyl iodide (Table 4).

TABLE 4. Rate constants for the reaction between perylene anion radical and ethyl iodide in DMF at 20°.

$[\text{CH}_3\text{CH}_2\text{I}]/\text{M}$	$\Delta E^C/\text{mV}$	$\log(k/\text{s}^{-1})$	$\log(k_2/\text{M}^{-1}\text{s}^{-1})$
0.0084	15	1.50	3.58
0.0168	20	1.80	3.58
0.0335	25	2.10	3.58
0.0838	30	2.40	3.48
0.1676	37.5	2.85	3.63
			ave. 3.57

Although this reaction is not of the ECE type as is the reaction between DPA cation radical and pyridine, application of eqn. (22) to the kinetic potential shift data resulted in second order rate constants nearly independent of the

ethyl iodide concentration. The latter indicates that the dependence of the magnitude of the potential shift on the rate constant is very nearly the same for the two mechanisms. Further work is necessary to verify the value assigned for the rate constant of this reaction. An alternative mechanism for the reaction is given by eqns. (24-25) in which the rate determining step is the atom transfer reaction. There is no firm evidence which rules this mechanism out and it appears more likely since even alkyl fluorides, which should be very hard to reduce undergo the reaction. Further work is in progress to attempt to differentiate between the two mechanisms.



The reaction of anthracene cation radical with pyridine is too rapid for rate determination by conventional techniques but was found to be amenable to the method described above. Rate data are summarized in Table 5. The second order rate constants were once again very nearly constant but showed a slight

TABLE 5. Rate constants for the reaction between anthracene cation radical and pyridine in MeCN at 20°.

[pyridine]/M	$\Delta E^C/\text{mV}$	$\log(k/\text{s}^{-1})$	$\log(k_2/\text{M}^{-1}\text{s}^{-1})$
0.0084	121	7.88	9.96
0.0211	130	8.40	10.08
0.0422	136	8.78	10.15
0.0844	142.5	9.15	10.22
			ave. 10.1

increase with increasing pyridine concentration. The value of the rate constant is very nearly that for a diffusion controlled reaction. A comparison was made between the reactions of DPA and anthracene cation radicals to determine whether or not a second order rate constant of  $10^{10} \text{ M}^{-1}\text{s}^{-1}$  is reasonable for the reaction between anthracene cation radical and pyridine. Anthracene cation radical reacts with acetonitrile as solvent with a first order rate constant of  $125 \text{ s}^{-1}$  (Ref. 42). DPA cation radical does not appear to react with acetonitrile at all so the very minimum possible half life was set at 24 hrs. which gives a maximum pseudo first order rate constant of  $10^{-5}\text{s}^{-1}$ , seven orders of magnitude smaller than that for anthracene cation radical. Since the second order rate constant for the reaction of DPA cation radical with pyridine is equal to  $2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  it was concluded that a rate constant for the anthracene cation radical/pyridine reaction equal to  $10^{10} \text{ M}^{-1}\text{s}^{-1}$  is a reasonable value.

The rate constant for the reaction between perylene anion radical and acetic acid has been determined to be equal to about  $10^2 \text{ M}^{-1}\text{s}^{-1}$  by double step chronoamperometry (Ref. 39). This reaction is too slow to be studied by the shift in the second harmonic crossing potential. The dianion of perylene reacts much more rapidly with proton donors and it was possible to study the reaction with acetic acid in spite of the fact that the latter is more easily reduced than is perylene dianion. Kinetic data are given in Table 6. The data are less reproducible than those in previous cases but show no trend with increasing concentration. The poorer reproducibility could be due to the fact that hydrogen gas from the reduction of acetic acid was being evolved at the electrode and made the potential measurements less certain. It should also be pointed out that the mechanism for this reaction differs from the previous cases in that this is a simple EC reaction while the others involved the transfer of two electrons by the ECC type scheme illustrated by eqns. (18-21).

The relative reactivities of the anion radical and the dianion can be compared in order to assess whether or not the rate constant determined is a reasonable value. The second order rate constants for the reaction of a number of aro-

TABLE 6. Rate constants for the reaction between perylene dianion and acetic acid in DMF at 20°C.

[HOAc]/M	$\Delta E^C$ /mV	$\log(k/s^{-1})$	$\log(k_2/M^{-1}s^{-1})$
0.0117	105	6.90	8.83
0.0233	120	7.80	9.43
0.0467	122.5	7.95	9.28
			ave. 9.18

matic anion radicals with water in DMF have been reported. Pyrene anion radical which is similar in structure to perylene anion radical was reported to have a second order rate constant of about  $10^{-3}M^{-1}s^{-1}$  (Ref. 43). Taking this as a rough estimate of the rate constant for the reaction between perylene anion radical and methanol in DMF allows one to estimate the relative reactivity of the anion radical and dianion. The rate constant for the reaction between perylene dianion and methanol in DMF has been estimated to be equal to  $10^5 M^{-1}s^{-1}$  (Ref. 28) which gives an estimate of  $10^8$  for the relative reactivity of the dianion and the anion radical toward proton donors. The rate constant given in Table 6 is  $10^7$  times greater than that determined for the reaction between perylene anion radical and acetic acid which is well within the limits of error for the estimation of the relative reactivity.

It has previously been mentioned that the formation of dianions, such as those from p-dinitrobenzene and benzophenone, in the presence of hydroxylic compounds is accompanied by a shift in the reversible potential to less negative values. This complicates the measurement of rate constants between dianions and the proton donors when the potential shift is being used to determine the rate. Under these conditions plots of  $\Delta E^C$  vs. proton donor concentration are not linear and the calculated second order rate constant increases with increasing concentration. This is demonstrated by data for the reaction of perylene dianion with methanol in DMF tabulated in Table 7. In order to estimate the

TABLE 7. Shifts in the reversible potential during the reaction of perylene dianion with methanol in DMF at 20°C.

[MeOH]/M	$\Delta E^C$ /mV	$\log(k/s^{-1})$	$\log(k_2/M^{-1}s^{-1})$	$\Delta E^{rev}$ /mV
0.008	37.5	2.85	4.94	0
0.016	45	3.30	5.10	3
0.040	60	4.20	5.60	11
0.081	72.5	4.95	6.04	18
0.162	90	6.00	6.79	31

magnitude of the shift in the reversible potential, the calculated second order rate constant at the lowest concentration of methanol was taken to be the correct value. Shifts in the reversible potential could then be calculated from the observed shift and the expected first order rate constant.

Preliminary results indicate that the kinetic shifts in potentials due to second order reactions, for example the dimerization of tropyli radical, are also linearly related to the rates of the reactions and can be treated similarly to the first order case (Ref. 44).

The linear relationship between the kinetic potential shift and the first order rate constants is predicted by theory. At a constant value of the voltage sweep rate, eqn. (16) can be rearranged to a form similar to (22). Similarly, inspection of Fig. 3 in ref. (30) leads to the conclusion that the second harmonic ac peaks and minima are shifted linearly with  $\log k$  when  $k$  is

large compared to  $\omega$ , a shift of the order of 28 mV per decade being predicted. The experimentally observed shift, *i.e.* the inverse of the slope in eqn. (22) is about 16.7 mV. Thus, theoretical calculations predict the form of the relationship but do not give the correct numerical values in the cases that have been tested here. Therefore, the empirically determined eqn. (22) appears to have sound theoretical justification and gives reliable rate constants for reactions too rapid to make measurements on by most other electrochemical techniques. Further work is in progress to determine the numerical values associated with eqn. (22) more precisely and to test the applicability on a variety of reactions with known rate constants.

#### ESTIMATION OF REVERSIBLE POTENTIALS IN REACTING SYSTEMS

As mentioned earlier, a reversible potential is only obtained by second harmonic ac voltammetry when the I and Q components intersect at zero current. In practice, the rate of a follow-up reaction does not have to be very great before the measurement cannot be achieved. However, the shift of the symmetrical voltammogram, discussed in the last section, from the reversible potential is predictable and reliable estimates can be made. Equation (22) was used to calculate  $\Delta E^C$  as a function of the first order rate constant for the reaction following charge transfer and the values are summarized in Table 8. Very few reactions following charge transfer are expected to have rate

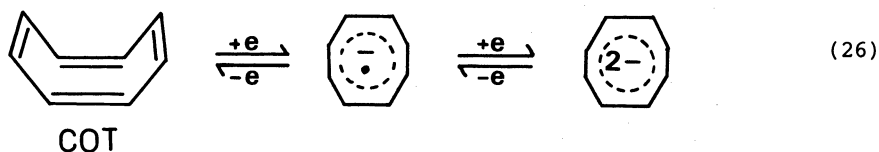
TABLE 8. Potential shifts as a function of rate constant.

$k/s^{-1}$	$\Delta E^C/mV$	$k/s^{-1}$	$\Delta E^C/mV$
10	7	$10^5$	73
$10^2$	23	$10^6$	90
$10^3$	40	$10^7$	107
$10^4$	57	$10^8$	123

constants exceeding  $10^8 s^{-1}$ . In most cases it should be possible to make a direct measurement of  $E^{rev}$  for reactions with rate constants of  $10^3 s^{-1}$  or less. This leaves those reactions having rate constants in the range  $10^4 s^{-1}$  to  $10^8 s^{-1}$ , with potential shifts of 60-120 mV, in doubt. Taking the latter into account allows one to estimate  $E^{rev}$  in practically all cases to about 50 mV from the correct value which is adequate for most applications. If the rate of the following reaction can be estimated to within two orders of magnitude,  $E^{rev}$  can be estimated with an uncertainty of 30 mV. The situation is even more favorable for estimating potentials for the formation of intermediates undergoing second order reactions.

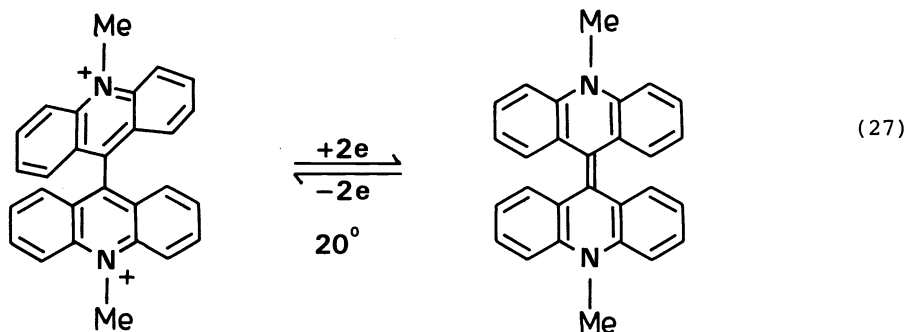
#### ELECTRON TRANSFER REACTIONS ACCOMPANIED BY CONFORMATION CHANGE

The reduction of cyclooctatetraene (COT) to the anion radical represents the classic case for this type of reaction. COT exists in a "tub" conformation in which the double bonds are localized. The anion radical and the dianion are expected to be planar or nearly so (Ref. 45). Allendoerfer and Rieger (Ref. 46) found that electron transfer to COT was slow compared to aromatic hydrocarbons and attributed the slow electron transfer to the energy barrier for COT to achieve a planar conformation. Quantitative data were obtained by Huebert and Smith (Ref. 47) who confirmed that the first electron transfer is slow and the second more normal (eqn. 26). Both of the studies



mentioned above were carried out in DMF containing either tetrabutylammonium or tetrapropylammonium ions. Two more recent studies (Refs. 48-49) have shown that the electron transfer rate to COT is very dependent upon the size of the supporting electrolyte cation and becomes reasonably fast in the presence of tetramethylammonium ion. These effects are not as yet completely understood.

A more extreme case of conformational change accompanying electron transfer is observed during the reduction of lucigenin dication ( $L^{2+}$ ) to dimethylbiacridine (DMB) shown in eqn. (27). The process was first believed to



involve a reversible one electron reduction of  $L^{2+}$  to  $L^+$  which then undergoes some sort of chemical reduction to DMB (Ref. 50).

We have reinvestigated the reaction and find that reduction in DMF is not a one electron process as previously believed (Ref. 50) but rather a quasi two electron process (Ref. 51). When the reduction was carried out in methylene chloride at  $-50^\circ$  the two one electron steps appear as discrete resolved steps in cyclic voltammetry as shown in Fig. 6. The dashed line represents the voltammogram measured at room temperature. Our interpretation of the voltam-

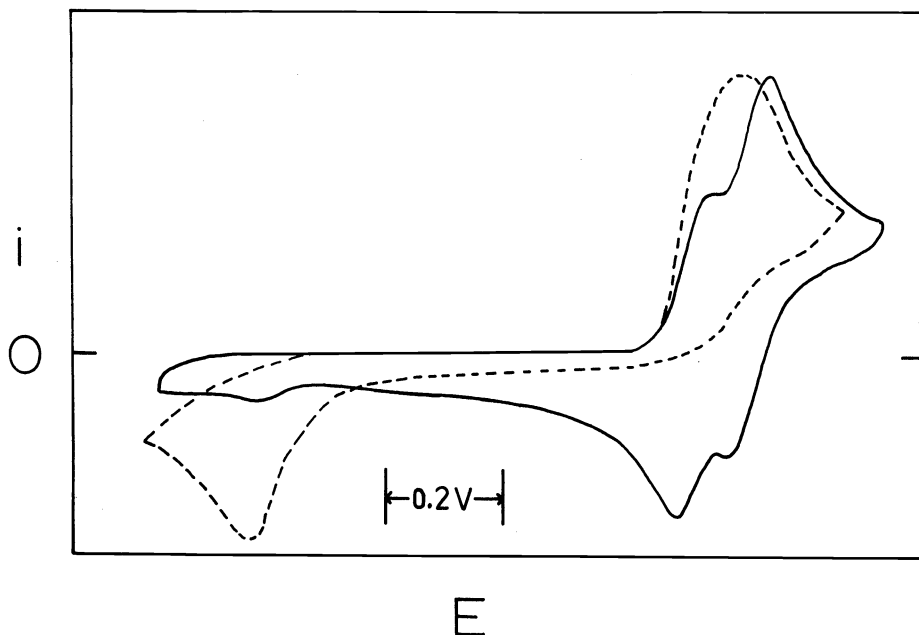
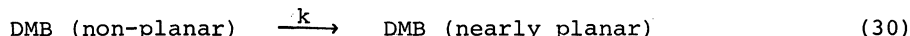
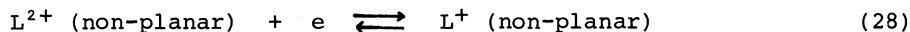


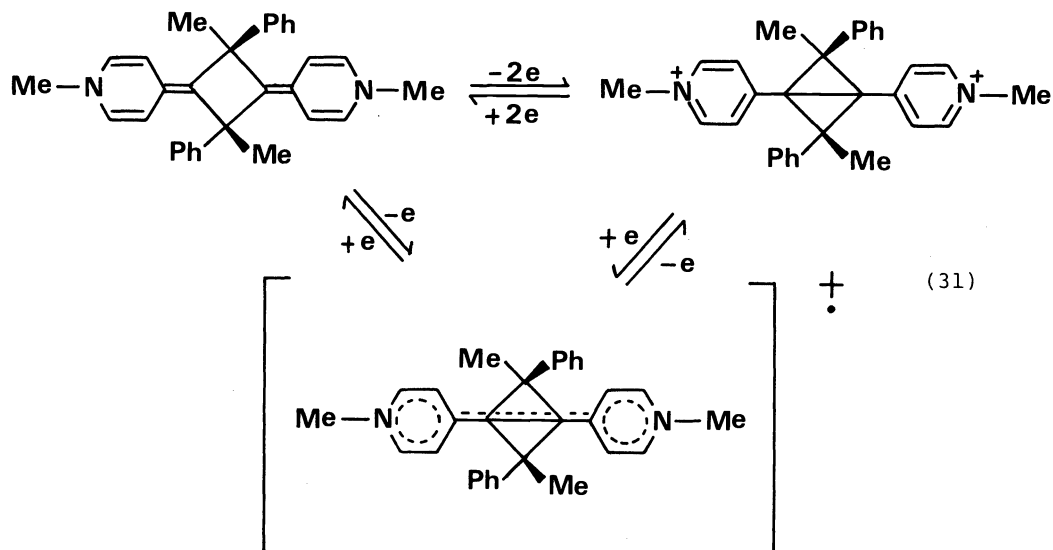
Fig. 6. Cyclic voltammogram of lucigenin dication in dichloromethane at  $-50^\circ$  (solid line) and at  $20^\circ$  (broken line) recorded at  $100 \text{ mVs}^{-1}$ .

mograms is shown in eqns. (28-30). At the electrode the two one electron steps are reversible to give first non-planar  $L^+$  and then non-planar DMB which is reasonably stable at  $-50^\circ$  but undergoes conformational change to give the nearly planar DMB at a rate depending upon the temperature.



There is severe interaction between the two rings and they are twisted out of plane but to a much lesser degree than the skew conformation in which the dication exists. The results indicate that the non-planar molecule is oxidized about 700 mV more easily than the near planar conformer. The non-planar molecule must have diradical character and further work, especially esr studies, is necessary to fully characterize the reaction.

A somewhat similar situation was encountered by Horner and Hünig during the voltammetric oxidation of a series of 1,3-bismethylenecyclobutanes (Ref. 52). The overall chemically reversible two electron oxidation to the bicyclobutane presumably proceeds by way of the formation of a cation radical in which the odd electron can be localized on either of the heterocyclic rings as indicated in eqn. (31).



It is apparent from the discussion above that slow electron transfer is not a good description of charge transfer coupled with large conformational changes. Even in the case of COT, which most likely involves a slow conformational change prior to electron transfer, the description is not very accurate. In fact if the conformational change were unfavorable enough, the electron transfer step would have to involve the tub conformation and would appear at much more negative potentials. An indication of this is that we have been unable to observe a reduction peak during attempted cyclic voltammetry measurements on the tetrabenzo-derivative which is expected to be much more rigid than COT itself.

#### CONCLUSION

I have attempted to summarize some of the aspects of electrode potential measurements which are relevant to the study of the thermodynamic and kinetic properties of aromatic ions and radicals generated at electrodes. The coverage has been biased toward my own research interests and is by no means exhaustive.

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