

# Steric Effects and the Electrochemistry of Phenyl-Substituted Anthracenes and Related Compounds

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The reduction and oxidation potentials of a series of phenylsubstituted anthracenes (9-, 9,10-, 1,9-, 1,10-, 1-, and 2-) and rubrene were determined by polarographic and cyclic voltammetric techniques. These potentials correlate well with those predicted by molecular orbital calculations, based on parameters obtained from the electron spin resonance spectra of the corresponding radical ions. These results lead to the conclusion that structural information, such as the angle between the phenyl substituent and the anthracene nucleus, can be obtained from electrochemical measurements. The mechanism of the protonation reaction following the electron transfer steps is shown to depend upon the electron density distribution and positions of substitution in the radical ions.

The electrochemical reduction and oxidation of aromatic hydrocarbons in aprotic solvents occurs by reversible one-electron additions or abstractions to the radical anions or cations.<sup>1</sup> The potentials at which these reductions and oxidations occur can be correlated to such parameters as electron affinities and ultra-violet absorption frequencies, as well as to energy levels calculated from molecular orbital theory.<sup>2</sup> In a previous study<sup>3</sup> we discussed electrochemical reduction of 9,10-diphenylanthracene (9,10-DPA), and showed that the reduction half-wave potential  $E_{\frac{1}{2}}$  could be calculated using the energy level obtained from an electron spin resonance (e.s.r.) investigation of the anion radical. Since the evaluation of the coupling constants in the e.s.r. spectrum of 9,10-DPA allowed an estimation of the steric effects in this molecule and the angle between the substituted phenyl rings and the anthracene nucleus,<sup>4</sup> this correlation between the reduction  $E_{\frac{1}{2}}$  and e.s.r. data suggested that electrochemical data could be used for studying steric effects. Polarographic data have been used previously to elucidate steric effects, particularly in nitro-substituted aromatic compounds.<sup>5</sup> Alternant aromatic hydrocarbons are particularly favourable for studying these effects however, because simple Hückel molecular orbital (HMO) theory has been shown to be successful in calculations with these kinds of molecules, the absence of heteroatoms allows calculations without the introduction of adjustable parameters, and e.s.r. investigations of both anion and cation radicals of these compounds are possible. The aim of this investigation was to extend the previous work on 9,10-DPA<sup>3</sup> to other related compounds and to examine further the electrochemical-e.s.r. correlation and the elucidation of steric effects from electrochemical data.

## EXPERIMENTAL

The purification of solvents and general techniques of the measurements have been described<sup>3,4</sup> Polarographic measurements were obtained with a 25-ml cell employing a dropping mercury electrode (dme) as working electrode, a mercury pool as auxiliary electrode and an aqueous saturated calomel electrode (S.C.E.), fitted with an agar plug and placed in a separate Luggin capillary compartment filled with test solution, as the reference electrode (fig. 1). The solutions for reductions were anhydrous N,N-dimethylformamide (DMF)

containing 0.10 M tetra-*n*-butylammonium iodide (TBAI) and were 1.5 mM in electroactive species. In a typical trial, doubly-distilled DMF was transferred volumetrically into the cell from a supply stored under nitrogen. This was de-aerated for 4 h with pre-purified nitrogen which had been passed successively through BTS-Katalysator, anhydrous magnesium perchlorate, activated charcoal at liquid-nitrogen temperature, and a pre-saturation vessel containing purified DMF. This lengthy de-aeration time and purification procedure was necessary to prevent the DMF solution from turning yellow upon addition of TBAI. The TBAI, mercury pool, dme, and reference electrode were added with nitrogen still flowing. Nitrogen flow was continued, over the solution, throughout the measurements.

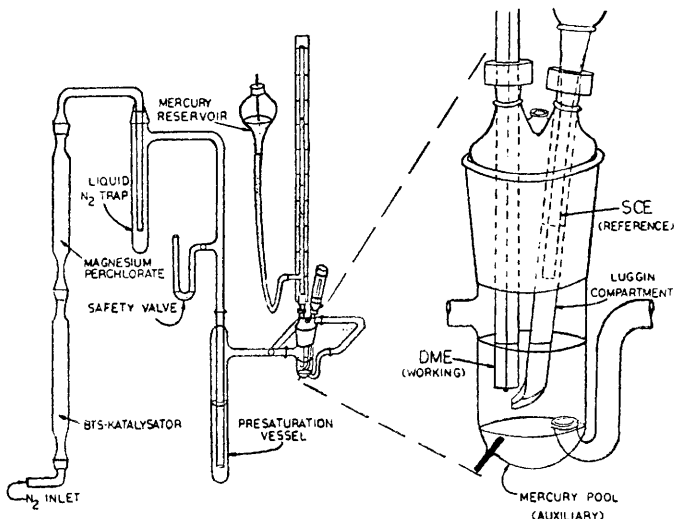


FIG. 1.—Cell and electrodes employed for polarographic measurement of reduction potentials.

The manual method of Meites<sup>6</sup> was used to determine  $E_{\frac{1}{2}}$ . The total cell resistance, between dme and mercury pool, was determined with an impedance bridge and was typically about 1 kohm. The uncompensated resistance between dme and the tip of the Luggin capillary was determined by impressing a small, known a.c. signal between the dme and the auxiliary electrodes, and finding the fraction of this signal appearing between dme and S.C.E., as described by Booman and Holbrook.<sup>7</sup> The correction resulting from uncompensated resistance was typically 1.3 mV. The error of measurement, estimated from the determination of  $E_{\frac{1}{2}}$  for anthracene on different days with different solutions, is probably 2 mV or less. Details of the apparatus and techniques are given by Maloy.<sup>8</sup>

The oxidation potentials were determined by cyclic voltammetry at a platinum disc electrode (0.031 cm<sup>2</sup>) in methylene chloride containing 0.20 M tetra-*n*-butylammonium perchlorate (TBAP). The instrument used for the measurements was provided with positive current feedback to compensate for resistance between the working electrode and reference electrode tip. Because of the lower accuracy of potential measurements using cyclic voltammetry and the fact that the potentials are a function of scan rate for some of the hydrocarbons, the potentials are reported only to the nearest 0.01 V.

## RESULTS AND DISCUSSION

The polarographic  $E_0$  values for the reduction in DMF and the oxidation in methylene chloride are shown in table 1. Also shown are values of  $m_{m+1}$  the root of the HMO secular equation corresponding to the lowest unoccupied  $\pi$  orbital, calculated using parameters obtained by fitting the e.s.r. spectrum of the anion radical of the hydrocarbon.<sup>4, 9</sup> For example, for 9-PA HMO calculations were performed assuming that the angle  $\theta$  between the phenyl-substituent and the anthracene nucleus

varied between 0 and 90°, and that the value  $\beta$  of the resonance integral for the bond between the phenyl ring and the anthracene nucleus was given by  $\beta = \beta_0 \cos \theta$ , where  $\beta_0$  is the resonance integral for the carbon-carbon bond in a planar system. The value of  $\beta$  (or  $\theta$ ) was determined from the best fit of the coupling constants of the ortho- and para- protons in the substituent phenyl ring. The value of  $m_{m+1}$  given is for this configuration. A similar procedure was used for 9,10-DPA. For 1,10-DPA, we assumed the angle of the phenyl in the 10-position was the same as that in 9-DPA, and varied the angle of the 1-position. For 1,9-DPA and R, the angles of all phenyl substituents were assumed equal.

The correlation between these  $m_{m+1}$  values and the reduction and oxidation  $E$  are shown in fig. 2 and 3. In making this correlation, we assume that  $\theta$  is essentially

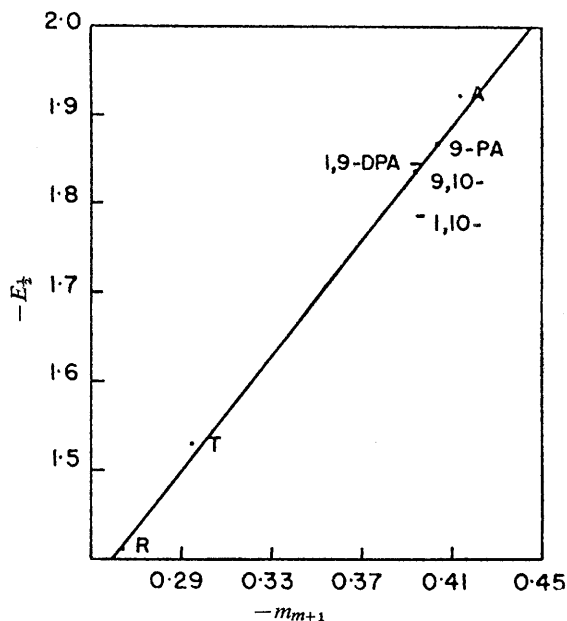
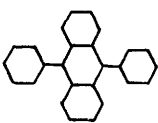
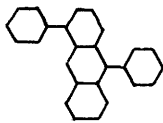
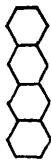
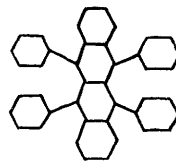


FIG. 2.—Half-wave potentials for the polarographic reduction of the aromatic hydrocarbons in DMF+0.1 M TBAI against energies of lowest vacant orbitals derived from e.s.r. measurements.

the same for the parent and the radical ion, so that the same  $m_{m+1}$  value applies to both. The good correlation obtained suggests that the measured  $E_{\frac{1}{2}}$ -values can be used to estimate  $\theta$ . The technique used is illustrated in fig. 4, which shows calculated  $E_{\frac{1}{2}}$  against  $\theta$  curves for different compounds, where  $E_{\frac{1}{2}}$  and  $m_{m+1}$  are correlated using  $E_{\frac{1}{2}}$  values of A and T to determine  $\beta_0$  and the other constants. Qualitatively, as  $\theta$  decreases and the compounds become more planar, more delocalization into the phenyl substituents becomes possible, and the compounds become easier to reduce. The trends for the angles in 9,10-DPA, 9-PA, 1-PA, and 2-PA are in the expected direction. The angle in 2-PA should be very similar to that of biphenyl. Biphenyl has a dihedral angle of about 42° in that vapour phase, as determined by electron diffraction,<sup>10</sup> and is essentially planar in the crystal state.<sup>11</sup> The value found here  $25 \pm 5^\circ$  is intermediate. However, in this case there may be considerable differences between the angles in the parent and radical anion, since the steric effect is small. Moreover, the difference between  $E_{\frac{1}{2}}$  for complete planarity and the quoted angle is only about 11 mV, so that there is a large uncertainty in the measurement.

TABLE 1.—REDUCTION AND OXIDATION POTENTIALS OF HYDROCARBONS

compounds	structure	$-m_{\text{H}} + 1^a$	$E_{\frac{1}{2}}(\text{red})^b$ V (S.C.E.)	$E_{\frac{1}{2}}(\text{oxd})^c$ oxidation V (S.C.E.)	sum $E_{\frac{1}{2}}(\text{red})$ + $E_{\frac{1}{2}}(\text{oxd})$	$\theta$
anthracene (A)		0.414	-1.920	1.34	-0.58	—
1-phenylanthracene (1-PA)			-1.878			53° <sup>e</sup>
2-phenylanthracene (2-PA)			-1.872			25° <sup>e</sup>
9-phenylanthracene (9-PA)		0.405 ± 0.002	-1.863	1.30	-0.56	68° <sup>d</sup>
1,9-diphenylanthracene (1,9-DPA)		0.394 ± 0.004	-1.846			60-70° <sup>d</sup>

9,10-diphenylanthracene (9,10-DPA)		$0.395 \pm 0.001$	-1.835	1.20	-0.64	$68^{\circ d}$
1,10-diphenylanthracene (1,10-DPA)		$0.398 \pm 0.004$	-1.787			$60-70^{\circ d}$
tetracene (T)		0.295	-1.530	0.95	-0.58	—
rubrene (R)		$0.264 \pm 0.004$	-1.410	0.78	-0.63	$60^{\circ d}$

(a)  $m_{m+1}$  calculated using e.s.r. fit; deviations shown represent uncertainties arising in fitting the e.s.r. spectrum.

(b) solution was DMF + 0.10 M TBAI at DME.

(c) solution was  $\text{CH}_2\text{Cl}_2$  + 0.20 M TBAP at platinum disc electrode.

(d) e.s.r. measurement.

(e) estimated from  $E_{1/2}$  for reduction.

It is also possible to correlate the measured  $E_{\frac{1}{2}}$  values with the ultra-violet absorption,  $p$ -bond frequency.<sup>12</sup> The correlation for the compounds in this study is shown in fig. 5; values of the  $p$ -band frequency are taken from the work of Dickerman and

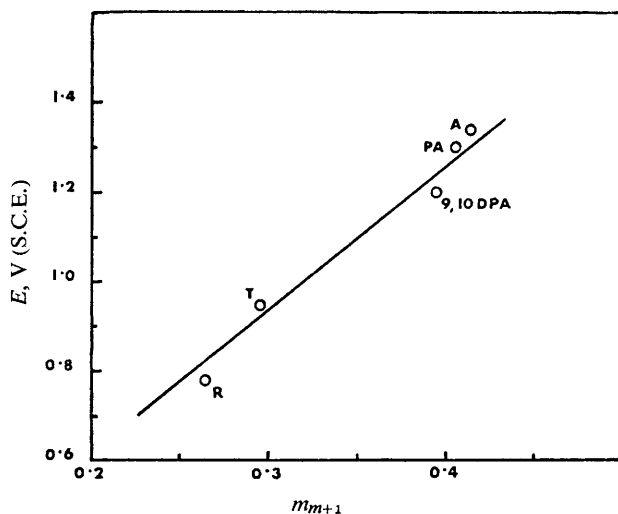


FIG. 3.—Half-wave potentials for the cyclic voltammetric oxidation of the aromatic hydrocarbons in MC+0.2 M TBAP against energies of highest occupied orbitals derived from e.s.r. measurements.

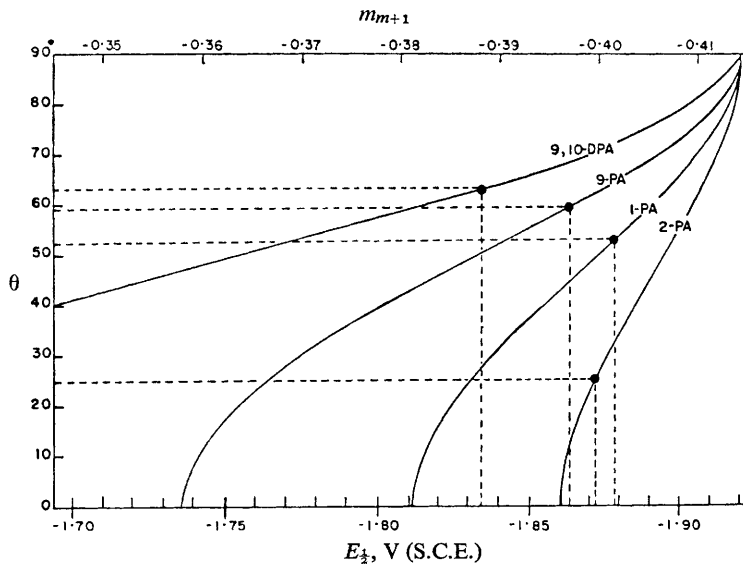
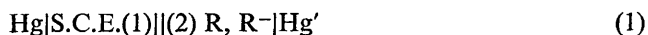


FIG. 4.—Variation of half-wave potentials for polarographic reduction with angle between phenyl substituent and anthracene nucleus.

co-workers.<sup>13</sup> The dimensionless slope of this line is 1.86; this value is close to the value predicted for alternant hydrocarbons, two  $[\Delta h\nu/\Delta E_{\frac{1}{2}} = (-2m\beta)/(-m\beta) = 2]$ .

If one considers the cell used in determining  $E_{\frac{1}{2}}(\text{red})$



where phase 1 is water and 2 is DMF -0.1 M TBAI, one can derive, using electrochemical potentials, the following equation :

$$E_{R,R}^{\circ'} = (\mu_R^{\circ 2} - \mu_{R^-}^{\circ 2})/F + E_j^{21} + c, \quad (2)$$

where  $\mu_R^{\circ 2}$  and  $\mu_{R^-}^{\circ 2}$  are the standard chemical potentials of R and R<sup>-</sup> in phase 2,  $E_{R,R}^{\circ'}$  is the formal potential for the reduction of R to R<sup>-</sup>,  $E_j^{21}$  is the liquid junction potential ( $E_j^{21} = \phi^2 - \phi^1$ , where  $\phi$  is the inner potential), and  $c$  is a constant containing the potential of the reference electrode (SCE). The term  $(\mu_R^{\circ 2} - \mu_{R^-}^{\circ 2})/F$  can be related to molecular orbital energy levels in the usual manner,<sup>2</sup> yielding

$$E_{R,R}^{\circ'} = -\alpha - m_{m+1}\beta_0 + [\mu_R^2(\text{solv}) - \mu_{R^-}^2(\text{solv})]/F + E_j^{21} + c, \quad (3)$$

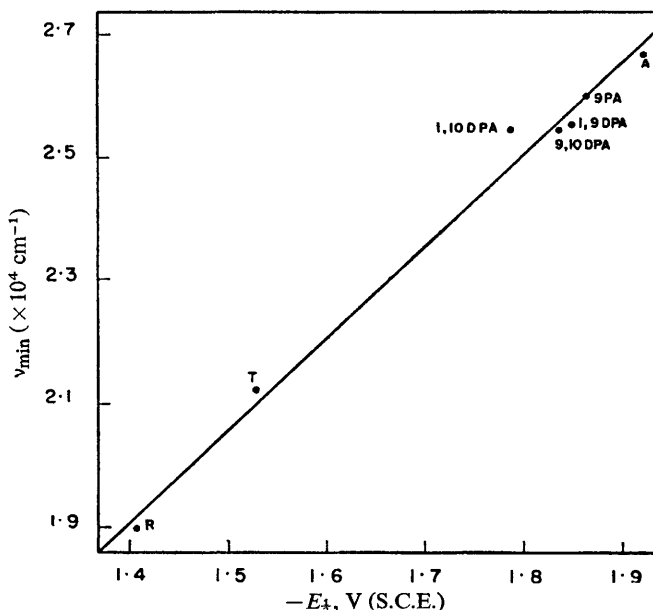
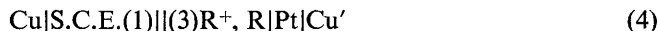


FIG. 5.—Half-wave potentials for the polarographic reduction of the aromatic hydrocarbons and the minimum(*p*-bond) ultra-violet absorption frequency. Spectroscopic data are for ethanolic solutions, except for rubrene, where the value in ethanol is estimated from data in solutions of similar refractive index.

where  $\mu_R^2(\text{solv})$  and  $\mu_{R^-}^2(\text{solv})$  are the standard free energies of solvation of R and R<sup>-</sup> in phase 2 and  $\alpha - m_{m+1}\beta_0$  is the energy of the lowest vacant m.o. In a similar manner, one can derive for the cell



where phase 3 in these experiments is CH<sub>2</sub>Cl<sub>2</sub> + 0.2 M TBAP, the expression

$$E_{R^+,R}^{\circ'} = -\alpha + m_m\beta_0 + [\mu_{R^+}^3(\text{solv}) - \mu_R^3(\text{solv})]/F + E_j^{31} + c, \quad (5)$$

where  $\alpha - m_m\beta_0$  is the energy of the highest occupied m.o.

The slope of the line in fig. 2, assuming that the  $E_{1/2}$ -values can be equated to the formal potentials (i.e., equal diffusion coefficients of parent and radical ion molecules), differences in free energies of solvation of R and R<sup>-</sup> are negligible, and  $E_j^{21}$  is constant, is then  $\beta_0^{-2}$ ; the value obtained, 3.16 eV is somewhat larger than that found in previous correlations of this type for a large number of hydrocarbons.<sup>1, 2</sup> Similarly, the slope in fig. 3 for oxidations is 3.41 eV; this value is less reliable, since the radical cations of A, 9-PA, and T are not very stable and the measured  $E_{1/2}$  is shifted in a negative

direction somewhat by the following chemical reaction. However, the stability of the cation radicals is probably greater in  $\text{CH}_2\text{Cl}_2$  than in acetonitrile.<sup>14</sup>

Eqn. (3) and (5) suggest that the sum  $E_{R^+,R}^{\text{O}'} + E_{R^-,R}^{\text{O}'}$  should be essentially constant for alternant aromatic hydrocarbons, where  $-m_{m+1} = m_m$ , if the solvation terms are about the same for all of the compounds. This approximate constancy of  $E_{\frac{1}{2}}(\text{red}) + E_{\frac{1}{2}}(\text{oxd})$ , shown in table 1, was also noted in a study of solvation energies of hydrocarbons in acetonitrile by Case, Hush, Parsons, and Peover.<sup>15</sup>

The overall path of the reduction of the phenyl-substituted anthracenes can also be predicted from electron density distributions based on molecular orbital calculations, following the suggestions of Hoijtink.<sup>16</sup> In all of the anthracenes the highest electron density is at the 9- and 10- positions, so that the attack by a proton donor on the radical anion or the dianion will occur here. For 9,10-DPA only two reduction waves, at  $E_{\frac{1}{2}}$  of  $-1.84$  and  $-2.46$  V (S.C.E.) are observed, because protonation of the dianion at the 9,10-positions yields a molecule with no conjugation between the four resulting phenyl rings. For 1,9- and 1,10-DPA however, three waves are observed with cyclic voltammetric  $E_p$  of about  $-1.93$ ,  $-2.40$ , and  $-2.80$  V (S.C.E.) (1,9-DPA) and  $-1.79$ ,  $-2.35$ , and  $-2.66$  V (S.C.E.) (1,10-DPA). This third wave arises because protonation in these molecules results in a biphenyl-like system; biphenyl itself is reduced in this medium at about  $-2.71$  V (S.C.E.).

The stability of the radical cations in  $\text{CH}_2\text{Cl}_2$  also depends upon whether or not the molecule is substituted in positions of high electron density.<sup>14</sup> Thus, 9,10-DPA and R form very stable cation radicals, while those of A and T are very unstable. 9-PA, which is substituted in only one of the two high electron density positions, is much more stable than A, but still undergoes a following chemical reaction.

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<sup>1</sup> This work has been reviewed in (a) M. E. Peover, *Electroanalytical Chemistry—A Series of Advances*, vol. 2, A. J. Bard, ed., (Marcel Dekker, Inc., New York, N.Y., 1967), chap. 1; (b) G. J. Hoijtink, *Ric. Sci. Suppl.*, 1960, **30**, 217.

<sup>2</sup> see e.g., (a) A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, (John Wiley and Sons, Inc., New York, N.Y., 1961), pp. 173-187; (b) R. Zahradnik and C. Parkanyi, *Talanta*, 1965, **12**, 1289 and references contained therein.

<sup>3</sup> K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, 1966, **88**, 2669.

<sup>4</sup> L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Physic. Chem.*, 1967, **71**, 223.

<sup>5</sup> see e.g., (a) D. H. Geske, J. L. Ragle, M. A. Bambenek and A. L. Balch, *J. Amer. Chem. Soc.*, 1964, **86**, 987; (b) B. von Zanten and W. Nauta, *Rec. trav. chim.*, 1961, **80**, 181; (c) P. Zuman, *Coll. Czech Chem. Comm.*, 1962, **27**, 649, and references contained therein.

<sup>6</sup> L. Meites, *J. Amer. Chem. Soc.*, 1950, **72**, 2293.

<sup>7</sup> G. L. Booman and W. B. Holbrook, *Anal. Chem.*, 1963, **35**, 1793.

<sup>8</sup> J. T. Maloy, *M.A. Thesis*, (The University of Texas, 1967).

<sup>9</sup> (a) L. O. Wheeler and A. J. Bard, *J. Physic. Chem.*, 1967, **71**, 4513. (b) L. O. Wheeler, *Ph.D. Diss.* (The University of Texas, 1967).

<sup>10</sup> A. Almenningen and O. Bastiansen, *Det. Kegl. Norske. Viden. Selsk. Skrofter*, no. 4, 1958, (*Chem. Abstr.* **53**, 11917).

<sup>11</sup> (a) J. Trotter, *Acta Cryst.*, 1961, **14**, 1135; (b) A. Hargreaves and S. H. Rizvi, *Acta Cryst.*, 1962, **15**, 365.

<sup>12</sup> (a) A. T. Watson and F. A. Matsen, *J. Chem. Physics*, 1950, **18**, 1305; (b) I. Bergman, *Trans. Faraday Soc.*, 1954, **50**, 829; 1956, **52**, 690.

<sup>13</sup> S. C. Dickerman, D. DeSouza and P. Wolf, *J. Org. Chem.*, 1965, **30**, 1981.

<sup>14</sup> J. Phelps, K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, 1967, **89**, 1752.

<sup>15</sup> B. Case, N. S. Hush, R. Parsons and M. E. Peover, *J. Electroanal. Chem.*, 1965, **10**, 360.

<sup>16</sup> (a) G. J. Hoijtink, *Rec. trav. chim.*, 1957, **76**, 775; (b) ref. (2a), pp. 425-431.