Solvent Effect on the Disproportionation of the Tetrakis-*p*-methoxyphenylethylene Cation Radical. An Experimental Verification of Theory

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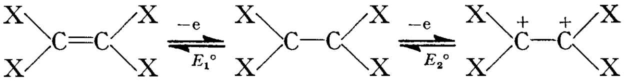
The disproportionation equilibrium, $2\ \mathrm{TME}^{+\cdot} \overset{K}{\rightleftharpoons} \mathrm{TME}^{2+} + \mathrm{TME}$, where TME is tetrakis-*p*-methoxyphenylethylene, was observed to be profoundly influenced by the fraction of acetonitrile present in dichloromethane–acetonitrile mixtures. In going from pure acetonitrile to pure dichloromethane, *K* decreased from 1·1 to 0·03. In the mixed solvent system, peak voltammograms show increasing peak width with increasing fraction of dichloromethane. Differences in E^0 for the two charge transfers were estimated from the voltammetric peak widths and disproportionation equilibrium constants were calculated. The plot of log *K versus* % acetonitrile was found to be linear over the entire range of solvent composition. Both the cation radical and dication were found to be stable in the solvent mixtures which had been passed over neutral alumina. Disproportionation equilibrium constants calculated from the visible absorption spectra of partially oxidized solutions of TME were nearly identical with the values predicted from analysis of the voltammetric peak widths.

VOLTAMMETRIC data obtained at stationary solid electrodes for the oxidation or reduction of organic compounds in aprotic media are potentially very useful in establishing reaction mechanisms involving homogeneous electron transfer reactions. We have recently examined the accuracy of calculation of equilibrium constants for the equilibration of stable aromatic cation radicals with aromatic compounds [equation (1)] and have found

$$\mathrm{Ar_1}^{+\cdot} + \mathrm{Ar_2} \overset{K}{\rightleftharpoons} \mathrm{Ar_1} + \mathrm{Ar_2}^{+\cdot} \qquad (1)$$

that peak potential differences could be used as reliable estimates of E^0 differences and equilibrium constants calculated from the Nernst equation agreed well with those determined spectrophotometrically.[1]

One of us has earlier suggested that the voltammetric oxidation of tetrakis-*p*-methoxyphenylethylene (TME) in acetonitrile, nearly but not quite, fits the criteria for a reversible two electron transfer.[2] The deviation from reversibility which was noted [2] was that the peak width $E_p - E_{p/2}$ was greater than the theoretical value. Later, Bard and Phelps [3] cited a theoretical study,[4] which appeared after our paper,[2] concerning the calculation of $E_2{}^0 - E_1{}^0$ for consecutive one electron transfers from overlapping waves in stationary electrode voltammetry, as an indication that the oxidation of TME actually



TME TME$^{+\cdot}$ TME^{2+} (2)

$X = p\text{-MeOC}_6\text{H}_4$

involved two closely spaced one electron transfers. A peak width of 43 mV was reported and an E^0 difference

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[1] U. Svanholm and V. D. Parker, *J.C.S. Perkin II*, 1973, 1594.

[2] V. D. Parker, K. Nyberg, and L. Eberson, *J. Electroanalyt. Chem.*, 1969, **22**, 150.

[3] A. J. Bard and J. Phelps, *J. Electroanalyt. Chem.*, 1970, **25**, App. 2.

[4] R. L. Meyers and I. Shain, *Analyt. Chem.*, 1969, **41**, 980.

of 8 mV was calculated,[3] *i.e.*, the cation radical ($TME^{+\cdot}$) was proposed to oxidize 8 mV more anodic than TME [equation (2)].

Since there was not complete agreement in the two sets of previous voltammetric data [2,3] and this system is ideally suited to check the applicability of the theoretical study,[4] we have undertaken a re-examination of the voltammetric behaviour of TME in acetonitrile, dichloromethane, and mixtures of the two solvents and have compared spectrophotometric equilibrium constants with those calculated from voltammetric data.

Voltammetry of TME.—The cyclic voltammetric behaviour of TME in acetonitrile [2,3] and in dichloromethane [3] has previously been described in detail and need not be repeated here. In mixtures of the two solvents, both the peak width ($w = E_{pa} - E_{pa/2}$) and the peak separation ($E_{pa} - E_{pc}$) becomes increasingly smaller as the fraction of acetonitrile is increased. Voltammetric data obtained at a Beckman platinum button electrode (39273) at a voltage sweep rate of 156 mV s^{-1} are summarized in Table 1. It was found that a plot of log (w — 29 mV) *versus* % acetonitrile in dichloromethane gave a linear plot over the entire range of solvent composition (Figure 1).

TABLE 1

Voltammetric data for oxidation of TME in dichloromethane–acetonitrile

MeCN in CH_2Cl_2 (%)	$E_{pa} - E_{pa/2}$/mV	$E_{pa} - E_{pc}$/mV
0	130	145
14	105	115
17	100	110
20	95	105
25	85	90
33	75	80
50	64	65
67	55	50
75	52	47
80	50	43
86	47	44
100	45 †	43 †
100	40—50	37—50

† Most frequently observed values. In MeCN, peak widths as low as 40 mV and peak separations as low as 37 mV were observed; however reproducibility was poor. This problem was not encountered in the mixed solvent and values of both quantities were readily reproducible.

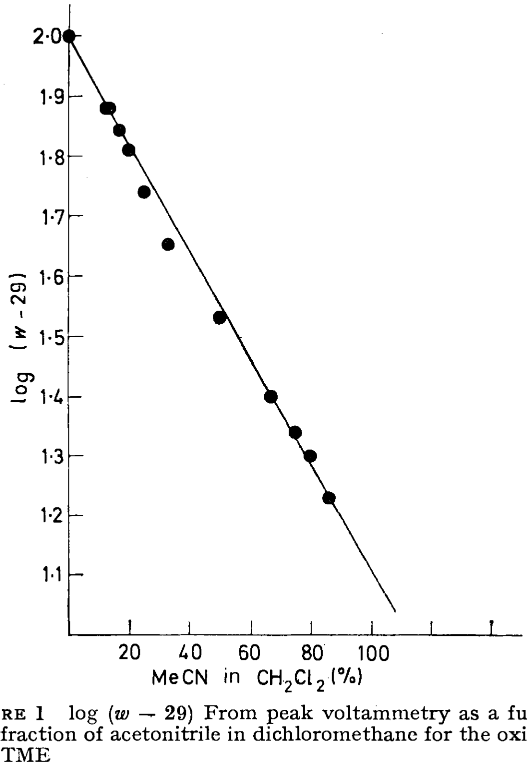

FIGURE 1 log (w — 29) From peak voltammetry as a function of fraction of acetonitrile in dichloromethane for the oxidation of TME

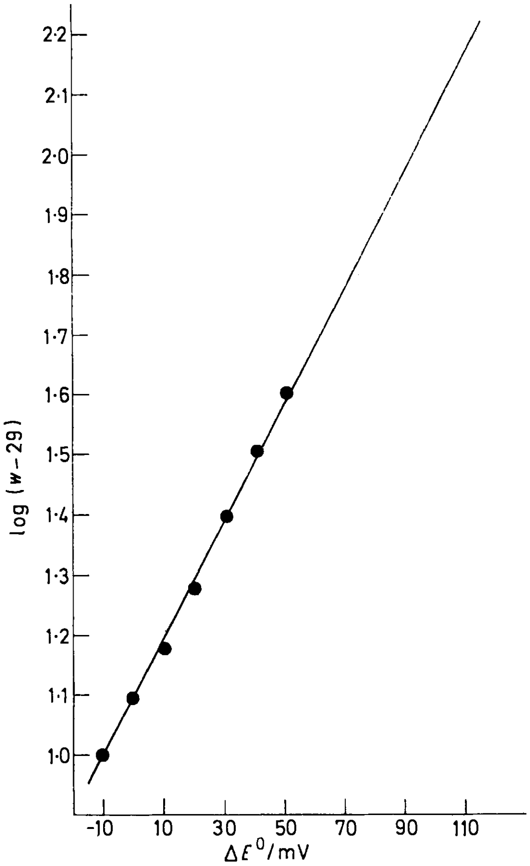

FIGURE 2 log (w — 29) As a function of $\Delta E°$ of closely spaced electron transfers

Re-plot of Results of Theoretical Calculations.—Myers and Shain have tabulated calculated values of ΔE^0 *versus* peak width for voltammograms of compounds undergoing successive electron transfers.[4] We find that their data can be reduced to linear form by plotting log (w — 29 mV) *versus* ΔE^0. Thus the range of the values given [4] can be extended to include the larger peak widths observed in this work. The data are plotted in Figure 2.

Preparation of Equilibrium Mixtures of TME, $TME^{+\cdot}$, and TME^{2+}.—The solvent or solvent mixture was passed through a column of neutral alumina (Woelm W 200) directly into the electrolysis vessel which contained TME and sodium perchlorate. When the supporting electrolyte was tetra-n-butylammonium fluoroborate (in mixtures containing <50% acetonitrile) the solvent mixture containing the supporting electrolyte was passed over alumina. The exact concentration of TME was determined from the magnitude of the limiting current at the rotating disc electrode. Oxidation at a platinum gauze electrode was carried out at constant current to a predetermined conversion. The ratio of oxidized to reduced species was then determined from the ratio of anodic to cathodic current at the rotating disc electrode. The distribution of the current between the three species was that given by equations (3) and (4).

$$i_{\mathrm{L,a}} = i_{\mathrm{TME}} + i_{\mathrm{TME}^{+\cdot}} \qquad (3)$$

$$i_{\mathrm{L,c}} = i_{\mathrm{TME}^{+\cdot}} + i_{\mathrm{TME}^{2+}} \qquad (4)$$

The total concentration of all species was then determined from the sum of the anodic and cathodic currents. Solutions prepared in this way showed no signs of decomposition over several hours. The concentration of $\mathrm{TME}^{+\cdot}$ could be determined directly from absorption spectra at 920 nm at which wavelength neither of the other two species show absorption. The current due to $\mathrm{TME}^{+\cdot}$ could then be calculated from equations (3) and (4) and the currents due to TME and TME^{2+} could be determined and hence the concentrations of all three species were known. Current responses for all species were obtained by measurements on solutions of known concentration prepared as described below for the ions. Alternatively, the concentration of both $\mathrm{TME}^{+\cdot}$ and TME^{2+} could be calculated from absorption at 920 and 460 nm. Both species show absorption bands at 460 nm. A further indication that no decomposition of the equilibrium solutions occurred was given by the fact that TME could quantitatively be regenerated by cathodic reduction. That the solutions were truly equilibrium mixtures was shown by the time independence of the visible absorption spectra.

Visible Absorption Spectra of $\mathrm{TME}^{+\cdot}$ *and* TME^{2+}.—The spectrum of $\mathrm{TME}^{+\cdot}$ consisted of two maxima at 565 (log ε 4·26) and 920 nm (4·29) in dichloromethane. Solutions of $\mathrm{TME}^{+\cdot}$ for spectral measurements were prepared by partial oxidation of TME (10^{-2}M) in dichloromethane. The concentration of $\mathrm{TME}^{+\cdot}$ was determined by the magnitude of the limiting current at the rotating disc electrode. In order to determine the extinction coefficient of the cation radical, the spectrum of a solution of $\mathrm{TME}^{+\cdot}$ (10^{-4}M) was measured in dichloromethane containing TME (10^{-2}M). Under those conditions, the concentration of TME^{2+} was of the order of 4×10^{-8}M and contributed negligibly to the spectrum. It was not possible to obtain the spectrum of the pure cation radical in acetonitrile owing to the unfavourable equilibrium. The spectrum of TME^{2+} was measured under conditions where neither $\mathrm{TME}^{+\cdot}$ nor TME was present, which was accomplished simply by exhaustive oxidation. The spectrum showed maxima at 402 (log ε 4·46), 454 (4·40), 565 (4·55), and 630 nm (4·51) in both acetonitrile and in dichloromethane.

Equilibrium Constants for the Disproportionation of $\mathrm{TME}^{+\cdot}$.—At least five values of the equilibrium constant for equation (5) were determined by spectral analysis

$$2\mathrm{TME}^{+\cdot} \rightleftharpoons \mathrm{TME}^{2+} + \mathrm{TME} \qquad (5)$$

of equilibrium mixtures obtained by oxidizing TME to various degrees of conversion. Individual values were reproducible to ±5% in each of the solvent mixtures. Values calculated from spectral data along with rotating disc electrode limiting currents are tabulated in Table 2.

TABLE 2

Differences in E^0 (ΔE^0/mV) for the first and second electron transfers from TME in dichloromethane–acetonitrile

MeCN in $\mathrm{CH_2Cl_2}$ (%)	K_{spectral} [a]	$\Delta E^0_{\mathrm{spectral}}$ [b]	K_{voltamm}	$\Delta E^0_{\mathrm{voltamm}}$ [c]	$\Delta(\Delta E^0)$ [d]
0	0·037	84	0·028	92	+8
12·5	0·080	65	0·048	78	+13
25	0·13	52	0·070	68	+16
50	0·26	35	0·16	46·5	+11·5
62·5	0·34	28	0·25	36·5	+8·5
75	0·53	16	0·36	26	+10
87·5	0·95	1·3	0·58	14	+12·7
100	1·13	−3	0·84	4·5	+7·5
				Average	+10·9

[a] The equilibrium constant for the disproportionation; $2\,\mathrm{TME}^{+\cdot} \rightleftharpoons \mathrm{TME}^{2+} + \mathrm{TME}$, calculated from u.v. and visible absorption spectra. [b] Calculated from the equilibrium constants at 25°. [c] Determined from the peak width *versus* ΔE^0 plot (Figure 2) using the voltammetric data of Table 1. [d] The difference between the spectral and voltammetric ΔE^0 values. It is generally accepted that solid electrode potentials may be in ±5 mV error.

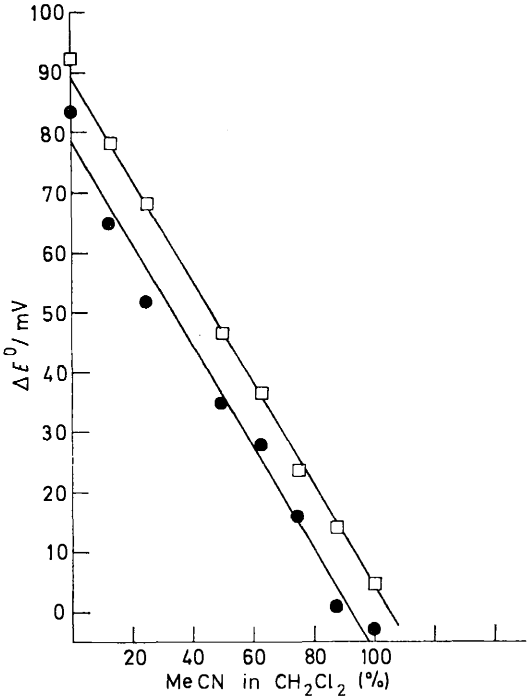

FIGURE 3 ΔE^0 For the oxidation of TME as a function of fraction of acetonitrile in dichloromethane: □, ΔE^0 from voltammetric data; ●, ΔE^0 from spectral data

Values of ΔE^0 calculated from the equilibrium constants ($\Delta E^0_{\mathrm{spectral}}$) are compared to values of ΔE^0 determined from the voltammetric data (Table 1) in conjunction with the plot of log (w − 29 mV) *versus* ΔE^0 (Figure 2). The two sets of ΔE^0 values are plotted *versus* fraction of acetonitrile in dichloromethane in Figure 3. Linear plots with nearly identical slopes are observed for the two sets of data.

DISCUSSION

The preliminary studies of the voltammetric oxidation of TME[2,3] resulted in conflicting viewpoints as to the nature of the electron transfer processes; *i.e.* ' direct ' two-electron *versus* consecutive one-electron transfers. There appears to be some confusion regarding the definition of these processes. First, let us examine what is meant by a ' direct ' two-electron transfer. It would appear to be virtually impossible that the second electron can be removed from the molecule before solvent reorganization around the cation radical takes place since the difference in the first and second ionization potentials is of the order of *ca.* 10 eV for oxidizable organic molecules. Thus, at the potential where the first electron is readily removed, solvent reorganization must occur before the second electron may be removed. In the event that solvation of A^+ [equation (6)] lowers the energy necessary for the removal of the second electron

$$A \underset{+e}{\overset{E_1^0 \atop -e}{\rightleftarrows}} A^+ \underset{+e}{\overset{E_2^0 \atop -e}{\rightleftarrows}} A^{2+} \qquad (6)$$

to the same potential as for the removal of the first, the following situation develops. At potentials where all A is oxidized at the electrode surface ($E_1^0 + 120$ mV for 99% conversion), rapid solvent reorganization around A^+ occurs and the second electron is transferred before diffusion of A^+ can take place. Thus, from an electrochemical point of view, a ' direct ' two-electron transfer has taken place, A diffuses to the electrode, A^{2+} diffuses away, and current corresponding to two electrons per molecule flows. But a complication enters with ΔE^0 *ca.* 0 ($\Delta E^0 = E_2^0 - E_1^0$). When the latter is the case, A^{2+} diffusing away from the electrode meets A and rapid disproportionation takes place generating A^+ which can diffuse to the electrode and undergo electron transfer. Thus, the process then becomes both a ' direct ' two-electron transfer from A mixed with a one-electron transfer from A^+. This situation results in broadening of the voltammetric peak during potential sweep voltammetry, characteristic of consecutive one electron transfers.

The question then arises, under what conditions are ' direct ' two-electron transfers observed? Consider first a one-electron oxidation of A following the Nernst equation. The concentration of A and A^+ at the electrode surface as a function of potential is shown in Figure 4. In region I, well cathodic of E_1^0, the current is virtually zero and the concentration of A^+ is negligibly small. In region II, the concentrations are determined by the Nernst equation while is region III all A is transformed to A^+, diffusion controlling the current. The same curves apply to the concentrations of A^+ and A^{2+} when we consider the second electron transfer at potentials around E_2^0. In region I, regardless of the value of ΔE^0, the number of electrons transferred from any one molecule undergoing oxidation is one. For example, if ΔE^0 is -100 mV; at a potential 200 mV cathodic of E_1^0, only 1 of 3,000 molecules at the electrode surface undergoes oxidation and only 1 of 55 of the oxidized molecules undergoes a second electron transfer. Thus, a one-electron transfer occurs to the extent of *ca.* 98%. Therefore, it would appear to be meaningful to discuss ' direct ' two *versus* consecutive one-electron transfers *only* at a potential (E_1^0 *ca.* $+120$ mV) where virtually all A is oxidized to A^+. At this potential, a second electron will be transferred providing that ΔE^0 is favourable (if ΔE^0 is $+60$ mV 9 in 10 molecules will undergo direct two-electron transfer while 999 of 1000 molecules will undergo ' direct ' two-electron transfer when ΔE^0 is -60 mV) and the electron transfers are fast relative to diffusion.

Meyers and Shain[4] have calculated the peak characteristics for voltammetry of species undergoing closely spaced consecutive electron transfers. It is obvious from the preceding discussion that similar peaks would be observed for molecules which undergo ' direct ' two-electron transfers accompanied by disproportionation equilibria in the diffusion layer. We have found that the calculated data[4] can be reduced to linear form by plotting log (w − 29 mV) *versus* ΔE^0. Thus, it appears that w − 29 mV, which may be regarded as a measure of the deviation from a voltammetric 2e peak, is a logarithmic function of ΔE^0 [equation (6)]. It is not obvious why this relationship should exist but it does make the calculated results more readily usable. From the plot (Figure 2), equation (7) can be derived. This

$$\log (w - 29) = (0{\cdot}00976)\Delta E^0 + 1{\cdot}095 \qquad (7)$$

equation holds to peak widths as low as 34 mV ($\Delta E^0 = -41$ mV) with large deviations from the calculated results appearing at smaller values of w. The upper limit for use of equation (7) is probably near the point where two separate peaks begin to emerge, at which point the equation is no longer necessary.

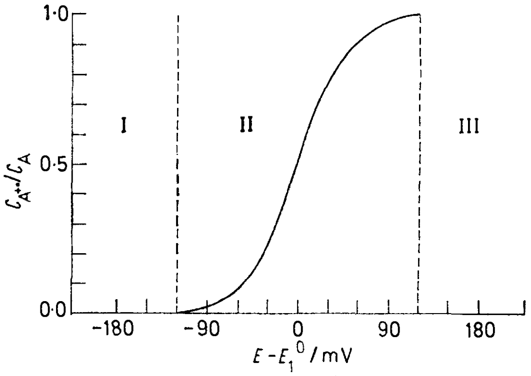

FIGURE 4 The ratio of oxidized to reduced species at the electrode surface as a function of electrode potential

A very interesting solvent effect is apparent from the voltammetery of TME in the mixed solvent system, dichloromethane–acetonitrile. log (w − 29 mV) Gives a straight line when plotted against % acetonitrile in dichloromethane. Thus, the deviation from 2e voltammetry decreases logarithmically as the fraction of acetonitrile is increased.[*] The latter is no doubt a reflection of the greater need for polar solvation of the dication than is necessary for the cation radical.

The dependence of ΔE^0 on the fraction of acetonitrile in dichloromethane was verified by the determination of the equilibrium constants for disproportionation of $\text{TME}^{+\cdot}$ [equation (5)] as a function of the solvent composition. In order to compare the two sets of experiments, the determined values of (w − 29 mV) were used to obtain estimates of ΔE^0 from the theoretical data (Figure 2). When the two sets of ΔE^0 values, *i.e.* the spectral and the voltammetric, were plotted *versus* solvent composition, straight lines were observed for both sets of data (Figure 3). The slopes of the two lines appear to be identical, with the ΔE^0 values estimated by voltammetry being 10·5 mV greater than those calculated from the spectrally determined equilibrium constants. A plausible explanation of the differences observed in the two sets of data is that ΔE^0 values calculated from the spectral data reflect the ratio of concentrations rather than activities and the activity coefficients of equation (8) may not cancel out. Discrepancies of greater magnitude, between voltammetrically and spectrally determined values for equilibrium constants for electron transfer reactions between cation radicals and aromatic compounds, have been observed.[1] In the latter case very close agreement was found when the four species [equation (1)] were of similar structure. However, when Ar_1 and Ar_2 differed substantially, discrepancies as great as 0·8 were observed in log K. The 10·5 mV deviation in ΔE^0 values observed in the present work represents only a difference of 0·18 between log K_{disp} calculated from the voltammetric and from the spectral data.

$$K_{\text{disp}} = \frac{(f_{\text{TME}^{2+}})C_{\text{TME}^{2+}}\,(f_{\text{TME}})C_{\text{TME}}}{(f_{\text{TME}^{+}}\,C_{\text{TME}^{+}})^2} \qquad (8)$$

The origin of the solvent effect must lie in the polarity changes taking place with the changes in solvent composition. The dielectric constant (D) of acetonitrile is 37 while that for dichloromethane is 9.[5] Since D is a colligative property, a linear increase in D of the solution is expected as the fraction of acetonitrile in dichloromethane is increased. It seems reasonable to predict that ΔE^0 for equation (2) should go to even lower values in solvents of higher dielectric constant.

EXPERIMENTAL

Reagent grade solvents were used. Acetonitrile was first purified by the method of Moe [6] and passed over neutral alumina before use. Dichloromethane was passed over neutral alumina immediately before use. Sodium perchlorate, oven dried and stored at 150°, was the supporting electrolyte in the mixed solvent while tetra-n-butylammonium fluoroborate was used in dichloromethane. In the latter case, the salt was dissolved in the solvent before the solution was passed over neutral alumina.

The apparatus for voltammetry was conventional and has previously been described.[7] Visible absorption spectra were recorded on a Unicam SP 800 spectrometer and equilibrium concentrations of $\text{TME}^{+\cdot}$ and TME^{2+} were determined from fixed wavelength measurements with a Beckman DU spectrophotometer.

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[*] For reasons which we are unable to explain, the cyclic voltammograms of TME in acetonitrile are not reproducible. In some cases in very dry acetonitrile, which had been passed over neutral alumina immediately before use, peak widths (w) as low as 40 mV and peak separations ($E_{\text{pa}} - E_{\text{pc}}$) as low as 37 mV were observed. Upon standing, the solutions gave voltammograms with much greater values of the two quantities. This problem was not encountered in the mixed solvent system. Thus, we feel that the most reliable value for w in pure acetonitrile is 42·5 mV, which is obtained by extrapolation of the data of Figure 1. The values of w previously reported in acetonitrile were 50 and 43 mV.[2,3]

[5] C. K. Mann, ' Electroanalytical Chemistry,' ed. A. J. Bard, Dekker, New York, ch. 2.

[6] N. S. Moe, *Acta Chem. Scand.*, 1967, **21**, 1389.

[7] O. Hammerich and V. D. Parker, *J.C.S. Perkin I*, 1972, 1718.